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13 ABSTRACT (Maximum 200 words)

A program directed toward a study of the Scanning Tunneling Microscope (STM) as a new instrument for examining and modifying surfaces at the atomic level. The STM has been developed to the point where it can be used routinely to record atomic surface structure and this technology has been successfully transferred to a commercial enterprise. The underlying technology can be used to mark surfaces on the scale of 100 Å exploiting a variety of physical mechanisms. The writing speeds and signal-to-noise ratios in this new marking technology are suitable for high density storage systems.

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Final Technical Report

covering the period

September 1, 1984 - August 31, 1990

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Metal-Vacuum-Metal Tunneling

Final Technical Report

September 1, 1984 - August 31, 1990

This document constitutes the Final Technical Report on the project that DARPA has supported over the past several years. The format differs from former reports. The report, itself, is a summary statement of the accomplishments at Stanford with the detail relegated to an in-depth paper that was written to cover the entire field of surface modification.

The goal of this project was to investigate the STM as a new tool in the field of digital storage. We wanted to understand the physical principles that underlie the operation of the STM, both in the linear mode of imaging and the non-linear mode of surface modification. The latter mode is used in the "writing" cycle and the linear mode is used in the "reading" cycle.

In recent years, well after this program was started, similar programs have appeared in many laboratories throughout the world. Major initiatives are underway in the US, in NATO, and in Japan; each with the aim of stimulating research in the area of fabricating nanometer-scale structures. The planned programs are based on the scanning probes in the STM family.

Our report is divided into two parts. The first part is a brief summary statement of the program at Stanford, and the second part is a statement on the programs outside of Stanford.

In addition, we have attached - as Appendix A - a review paper that covers the accomplishments in the entire field of surface modification. It contains much of the detail that is omitted in the summaries of Sections A and B.

A. Summary of the Work at Stanford

The work at Stanford was divided into three sections: (1) the effort to design and fabricate instruments based on the principles of scanning probes, (2) the effort to understand the physical mechanisms that underlie the imaging mode, and (3) the effort to find mechanisms for modifying the surface structure. We were searching for a method of using the scanning probes to mark the surface in a way suitable for high density storage of digital information.

In the first section, we were successful in building the instruments. These instruments, with the essence of the Stanford design, are now being offered as commercial units by Park Scientific Instruments of Mountain View, California.

In the second section, we gained wide experience in imaging on the surface of metals, semiconductors, and films of organic molecules deposited on smooth substrates. This experience has given us the understanding that we need to interpret most of the images that are now being recorded.

In the third section we have had success in "writing" small features in the surface of gold, in the surface of graphite and in films of organic molecules placed on the graphite surface. We have, also, found it possible to make a film of organic molecules overlying the graphite surface.

The most successful was the "writing" on graphite. We pulsed the tip voltage to 4 volts to create pits in the uppermost layer of graphite, pits 50-100 Å in diameter. This system is reliable to the point where we can write with an accuracy approaching 98%.

B. Summary of Related Work in Other Laboratories

Many laboratories throughout the world have undertaken work on surface modification with the scanning probes. Much of it is in the IBM Laboratories, but significant work has been done in Philips Research Laboratories and in other Universities.

This group has determined that patterns of fine dots (100 Å in diameter) can be written on gold, on silicon and on graphite. The "writing" is remarkably fast and reproducible. It would appear that the total sustained effort is sufficient to ensure that new technologies will emerge in the field of "nano-scale" structures.

Finally, we include the review paper that we have prepared on the emerging technology. It is written in such a way that others can appreciate what has been done to date. It provides the detail and background information that will be useful for those groups that want to enter this new field.

Appendix A

Manipulation and Modification of Nanometer Scale Objects with the STM

by

C. F. Quate

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Manipulation and Modification of Nanometer Scale Objects with the STM

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I. Introduction

The scanning probes associated with the STM are used in the fields of surface physics, surface chemistry and molecular biology. The images display electronic, atomic, and molecular structure.

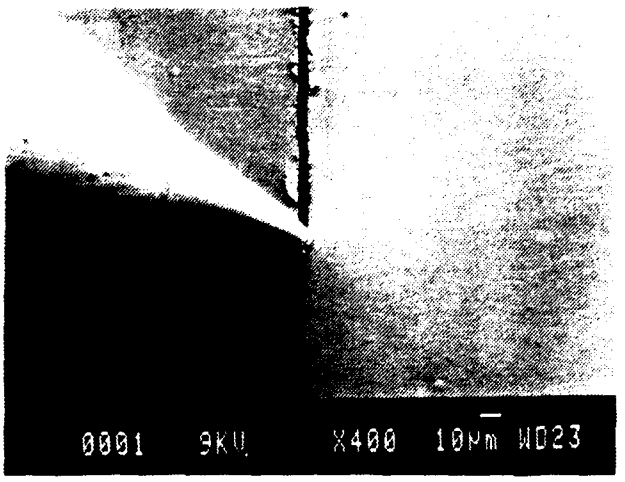
In this presentation we are not concerned with imaging. We are concerned with the generation of structure, the modification of surfaces and the manipulation of objects on these surfaces. We are interested in the "nano-scale" where structures have dimensions of nanometers.

In the summer of 1985, Gerd Binnig and Heini Rohrer convened a small meeting in Oberlech, Austria. At that meeting they commented on the diversity of the STM. We cannot improve on their description. They said[1] -- "This local probing capability, ..., make it increasingly attractive for use in diverse areas of science and technology, reaching beyond its initial use in atomic-scale imaging. In many applications, its primary role .... is used primarily to select and define the location of the experiment. In other applications, ..., imaging might not be used at all."

The illustration of Fig. 1 - a scratch in a gold film made with the tip of an STM - is a vivid reminder that the instrument is more than a device for imaging; it is a multi-function device with a power that extends beyond imaging.

The scanning probe, illustrated in Fig. 2, with its sharp tip and intense *E*-fields, can deposit, remove, and arrange surface atoms. It can reverse the direction of magnetization

(a)



(b)

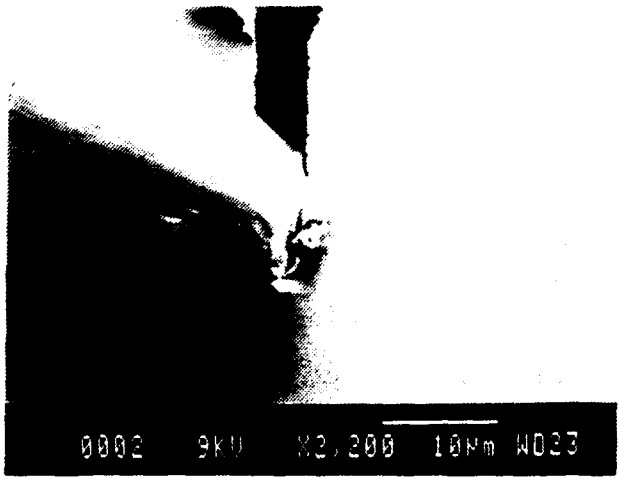


FIG. 1 (a) Scratch generated with the STM in a gold film 300 Å thick vacuum deposited on graphite

(b) Enlarged area indicating that the graphite substrate is still intact. [From H. Fuchs and R. Laschinski, "Surface investigations with a combined scanning electron-scanning tunneling microscope," *Scanning*, **12**, 126-132 (1990).]

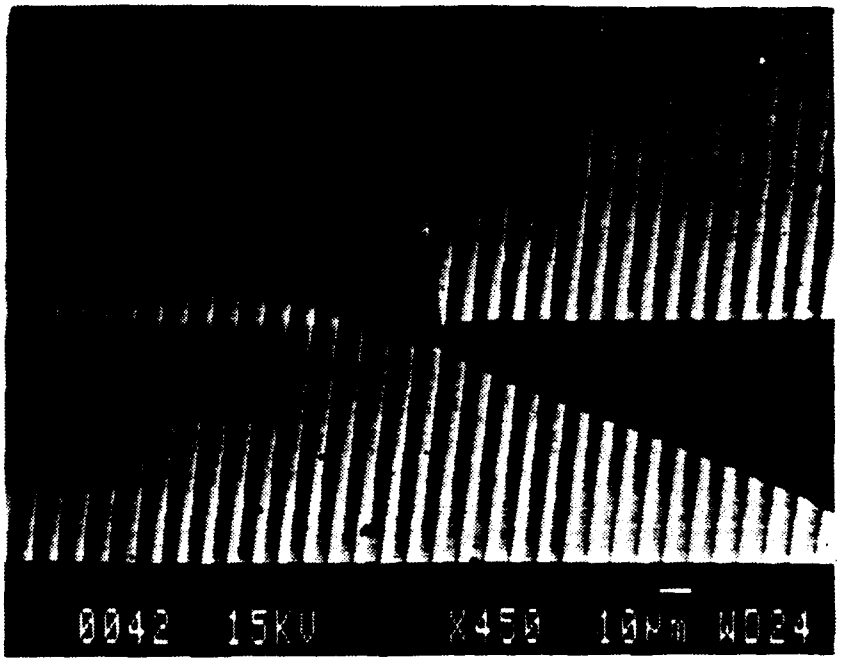


FIG. 2 The tip of the STM hovering over an optical grating etched in glass. [Courtesy of A. de Lozanne, University of Texas.]

in thin magnetic films. The energy in the tunneling electrons can be exploited to dissociate molecules, to attach molecules to substrates, to detach molecules from substrates, to raise the temperature above the melting point for materials with low thermal conductivity, and to enhance the reaction on the substrate for selected etchants. The forces associated with the tip can be used to move atoms along the surface of the substrate and to transfer atoms between the tip and substrate. The modification, and manipulation, takes place in a well controlled fashion over regions with nanometer dimensions. These probes are tools for performing experiments on the "local scale" in the small region at the end of the tip.

The modifications are examined with the scanning tip, itself. It is only necessary to operate the instrument in the imaging mode where the tip voltage is reduced to a minimum.

A report on this field was prepared for the NATO workshop held in Erice in the spring of 1989.[2] The results that have appeared in the intervening months are quite remarkable. In that short interval, devices - albeit primitive - have actually been fabricated.

We begin our discussion with the early attempts to modify surface structure by applying high voltage pulses to the tip positioned at precise locations on the sample.[3]

II. Gold Surfaces -- Initial Results

At the meeting in Oberlech, a group from Berkeley[4] discussed the modification of a gold surface with a tungsten tip of the STM. We quote from their article - "By lowering the tip to the surface we have been able to produce indentations typically 100 Å across; .... By operating the microscope at high tunneling current (...) and reduced gap spacing, we have been able to deposit material on the surface to form hillocks roughly 300 to 400 Å across and 12 Å high. In both surface-modification processes, surface diffusion was observed with a characteristic time of the order of minutes." This succinct statement, summarizing the important properties, established the ground for much that followed.

Their report did not generate the interest that it deserved. The exciting element, the focus of our primary interest at the Oberlech conference, was the atomic structure in many

of the images. The interest in the holes and gold hillock of Fig. 3 was limited. We will learn that this view was very short-sighted when we return to this subject in a later section.

Surface modification on the atomic scale was first demonstrated by Becker *et al.*[5] when they "wrote" on the surface of Ge(111) with the STM by increasing the bias on the tip to 4 volts. They discovered that this procedure would create atomic-scale hillocks on the germanium surface. The hillocks were approximately 1 Å in height and 8 Å in diameter. Their success rate for transforming the surface of germanium was improved when they moved the tungsten tip to a remote location on the Ge surface and deliberately touched the tip to the sample. They inferred from this that Ge atoms, adhering to the tip after touching, were transferred to the sample during the "writing" cycle. In effect, a field-induced transfer of atomic species across the gap from the tip to sample.

The report from Becker stands as the pioneering effort in "writing bits" on the atomic scale, but it was not the first attempt to modify surfaces with the scanning probes. That was done earlier by Ringger *et al.*[6] and McCord *et al.*[7] Ringger succeeded in "scratching" silicon by scanning while the tip was in virtual contact with the silicon surface. The recorded pattern was a series of parallel linear lines scribed in the hydrocarbon films covering their surfaces.

Hydrocarbon films are always present in those systems that use oil diffusion pumps for the vacuum. These films are easily polymerized when exposed to electron beams. The first report came from Stewart[8] working with electrons at 200 eV ... "In an evacuated tube in which the slightest traces of organic vapors may occur, ... insulating layers are formed on surfaces subject to electron ... bombardment. These layers may be attributed to carbon compounds and their formation is related to the polymerization of organic vapors ..."

Broers[9] demonstrated the utility of such a system for lithography in his work with the SEM.

In direct analogy with this, McCord *et al.* used the electrons from a scanning tip to polymerize hydrocarbon films. They used the scanning tip in the field emission mode with

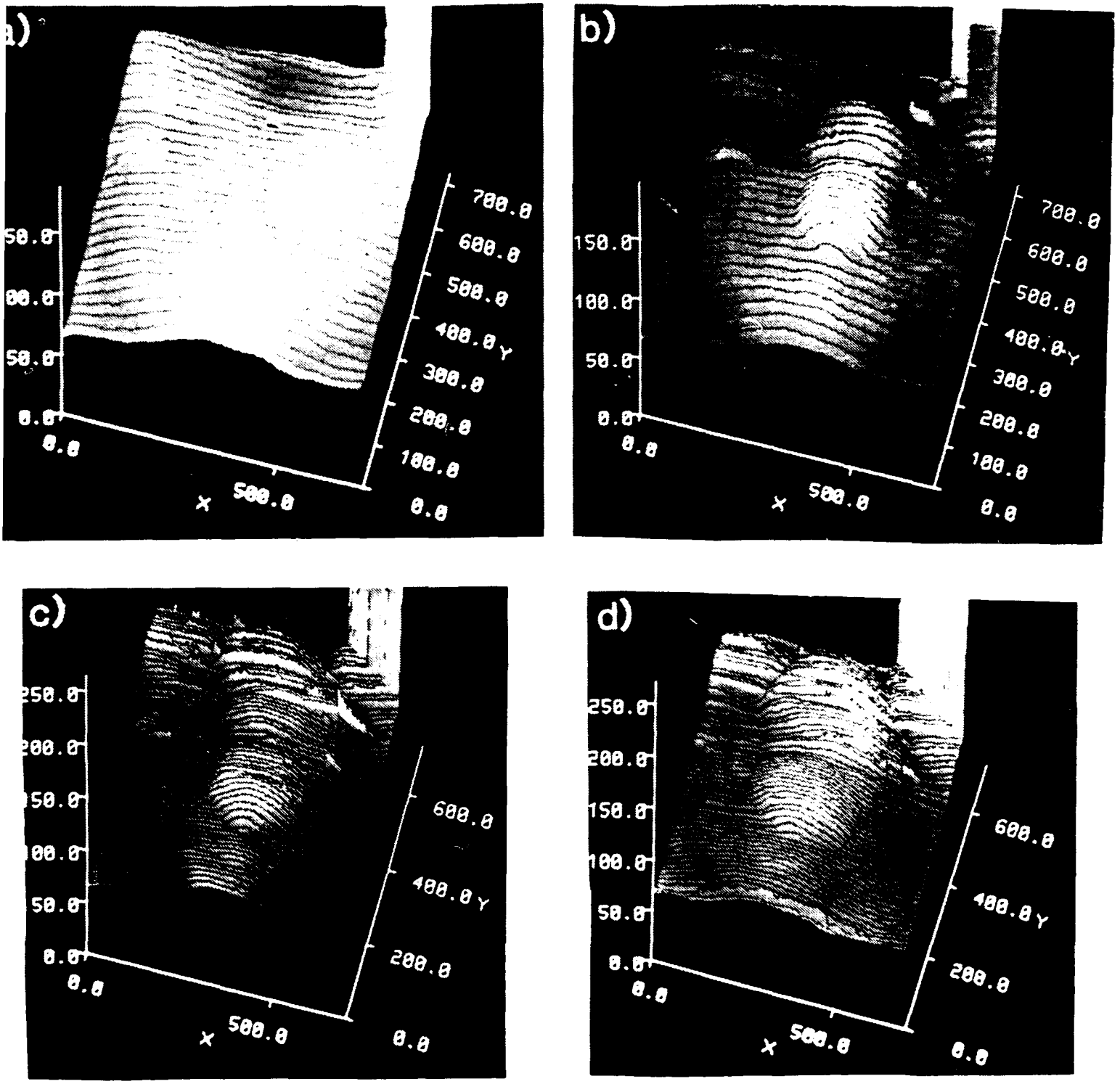


FIG. 3 Mounds on the polished surface (210) of a gold single crystal. The hillocks were produced by increasing the tunneling current to 1 μA with the tip positively biased at 5 mV. [From D. W. Abraham, H. J. Mamin, E. Ganz, and J. Clarke, "Surface modification with the scanning tunneling microscope," *IBM J. Res. Develop.* **30**, 492-499 (September 1986).]

a large spacing between tip and sample. The STM, modified in this way, resembles the scanning electron microscope. The tip was an intense source of electrons - "without space charge or aberrations." With a 10 volt bias on the tip they were able to form lines 1000 Å in width.

In a second experiment, they formed monolayers of docosenoic acid (CH_3 $(CH_2)_9$: $(CH_2)_{12}$ COOH) in a Langmuir-Blodgett trough and transferred the monolayers onto Al films (100 Å thick) vacuum deposited on silicon substrates. Docosenoic acid was chosen since it was known from prior work[10] that these films are easily exposed with electrons. McCord used electrons from the scanning tip at 25 volts to expose the monolayers. The Al in the unexposed areas was removed with wet etchants. The Al lines formed in this way were 1000 Å in width.

The field emission mode was also used by Marrian and Colton[11] to expose a film of polydiacetylene. Their films were prepared on silicon substrates in a Langmuir-Blodgett trough. Their tip was positioned close to the substrate within tunneling range. Whey they ramped the tip voltage to 10-20 volts they formed patterns on the substrate that were different from that reported by McCord. Their process occasionally produced depressions in the organic film but more often hillocks were formed and it was the hillocks that attracted most of their attention. They were 80 Å in height and 200-600 Å in diameter.

III. Mono-molecular Layers -- Langmuir-Blodgett and Self-Assembly

Organic films as monomolecular layers are easily formed on substrates. The established techniques[12] include: the Langmuir-Blodgett trough (LB), self-assembly (SA). depositing molecules from solution, and ordered layers formed at the interface between the substrate and a liquid-crystal. These films are obvious and natural candidates for modification with the STM at the local level, but the initial results are ambiguous and inconclusive. Nevertheless, there is a widespread perception that the potential in this field

is very strong. The continuing effort to exploit phenomena in this arena warrants attention in our review.

(a) Langmuir-Blodgett Films

In the LB technique, the molecules are spread on the surface of a liquid, compressed to form a contiguous film, and transferred to the substrate by dipping it through the compressed film. Bilayers of Cadmium-Arachidate, transferred to graphite, were the first organic molecules studied with the STM.[13] The molecules were arranged perpendicular to the substrate in a periodic array. The individual molecules in the STM images stood out from the background with strong contrast.

These films must be formed on a substrate that is smooth and flat on the atomic scale. Graphite has been extensively used for this purpose but it is not ideal; the surface is hydrophobic and inert. Film adhesion is problematical. Epitaxial gold grown on mica has often been used, but a preferred substrate, recently revealed by Fuchs, *et al.*[14], is WSe_2. The surface of Tungsten Diselenide is hydrophilic and molecular adhesion to the substrate is very good. Stable films of 22-tricosenoic acid covering large areas of the substrate are easily prepared. The ($CH = CH\text{-}(CH_2)_{20}\ COOH$) molecules, 32 Å in length, can be imaged more than two months after the films are laid down.

There is a problem with linear molecules arranged perpendicular to the substrate. The mechanism that gives rise to the current along the length of the molecules is not understood. The path along the linear chain is much too long for tunneling.

For parallel alignment, where the molecules lie parallel to the surface, the current can be explained with tunneling electrons moving across the narrow dimension of the molecule. An example of this comes from the work of Kuroda *et al.*[15] They used the LB trough to form a bilayer of behenic acid ($CH_3\ (CH_2)_{20}\ COOH$) on graphite. The images, recorded with a negative bias on the sample, indicate that the molecules are in registration with the graphite lattice.

Various polymer films [poly(methyl methacrylate) (PMMA) and poly(methyl pentene sulphone) (PMPS)] on graphite, prepared as thin films in a LB trough, have been studied by Dovek *et al.*[16,17] They used the STM to image and modify the structure of the molecules. Their images showed arrays of polymer fibrils lying parallel to the surface. There was no evidence for molecular order. These films are easily modified by applying a negative voltage pulse to the tip, 4 volts in amplitude and 0.1 microseconds in duration.

The modification of graphite can proceed without the overlying organic film. Albrecht[18] observed etch pits beneath the tip on clean graphite bathed in a vapor of water molecules. Rabe *et al.*[19] in his study of octylcyanobiphenyl on graphite reports that etch pits were created in graphite when the tip bias is raised abov ..5 V. They found that the pits were formed in air, in water vapor (10 mbar of pressure), and silicone oil as well as octylcyanobiphenyl. We will return to this subject in a later section for a more complete discussion.

(b) Liquid-Crystals

Foster and Frommer[20] have described a simple process for organizing molecular arrays on the surface of graphite. A small drop of liquid crystal, with cyanobiphenyl compounds as the major component, was placed on a heated graphite surface. The molecules are physi-absorbed onto the surface over a period of 1-2 hours. They discovered that the interaction at the interface changes the liquid-crystal molecules on the substrate described as "a two-dimensional solid crystal" by Mizutani *et al.*[21] The two benzene rings of each molecule were clearly displayed in many of the images. Their beautiful images of the molecules arranged in ordered patterns were easily simulated with molecular modeling.

A further study of these molecules by Smith *et al.*[22] confirmed the work of the Foster group. Smith went on to analyze the structural properties of a class of molecules labeled as 4'-*n*-alkyl-4-cyanobiphenyl (*m*CB, where $m = 8, 10, 12$ indicates the number of

carbons in the alkyl group). The molecular order, the components of the individual molecules, and the registry with the substrate lattice, were all examined in great detail.

In a second paper,[23] Foster's group raised the question of manipulating individual molecules. For that study they covered a graphite surface with di(2-ethylhexyl)phthalate and moved the tip toward the substrate into the tunneling range. The familiar atomic structure of graphite appeared in the image when the surface was scanned with the tip biased at 30 mV. When the tungsten tip was pulsed to a voltage of 4 volts for 1 microsecond a sizeable structure appeared on the surface. They thought that the structure was a molecule of phthalate chemically bonded to the substrate. The object could be removed by pulsing the tip a second time with the tip positioned directly above the object. The voltage threshold for both processes was 3.5 volts.

This system with the pinning and depinning of individual molecules is an attractive method for modifying surfaces. The energy from the tunneling electrons is sufficient to either form, or break, the chemical bond. However, this process is confused by questions of the type raised in the work described below.

(c) Alkanes Adsorbed on Graphite

Bernhardt *et al.*[24] took up the study of fabricating "nano-scale patterns" with the STM. They examined the system introduced by Foster and moved on to study ordered monomolecular layers of the *n*-alkanes. There is a great deal of background material in the literature relating to the adsorption on graphite of *n*-alkanes with chain lengths of 2 to 40 atoms. They used this information to adsorb a uniform ordered layer of *n*-$C_{32}H_{66}$ on graphite from a solution of *n*-$C_{10}H_{22}$ and 2-2-4 trimethylpentane (isooctane). The patterns were imaged with a Pt/Ir tip in the STM. The images, with fine detail in the molecular chains, indicated that the molecules were in registration with the graphite substrate.

They followed this with a series of experiments designed to produce the nanometer-scale features described by Foster's group. The work is best summarized with a sequence of four images of Fig. 4.

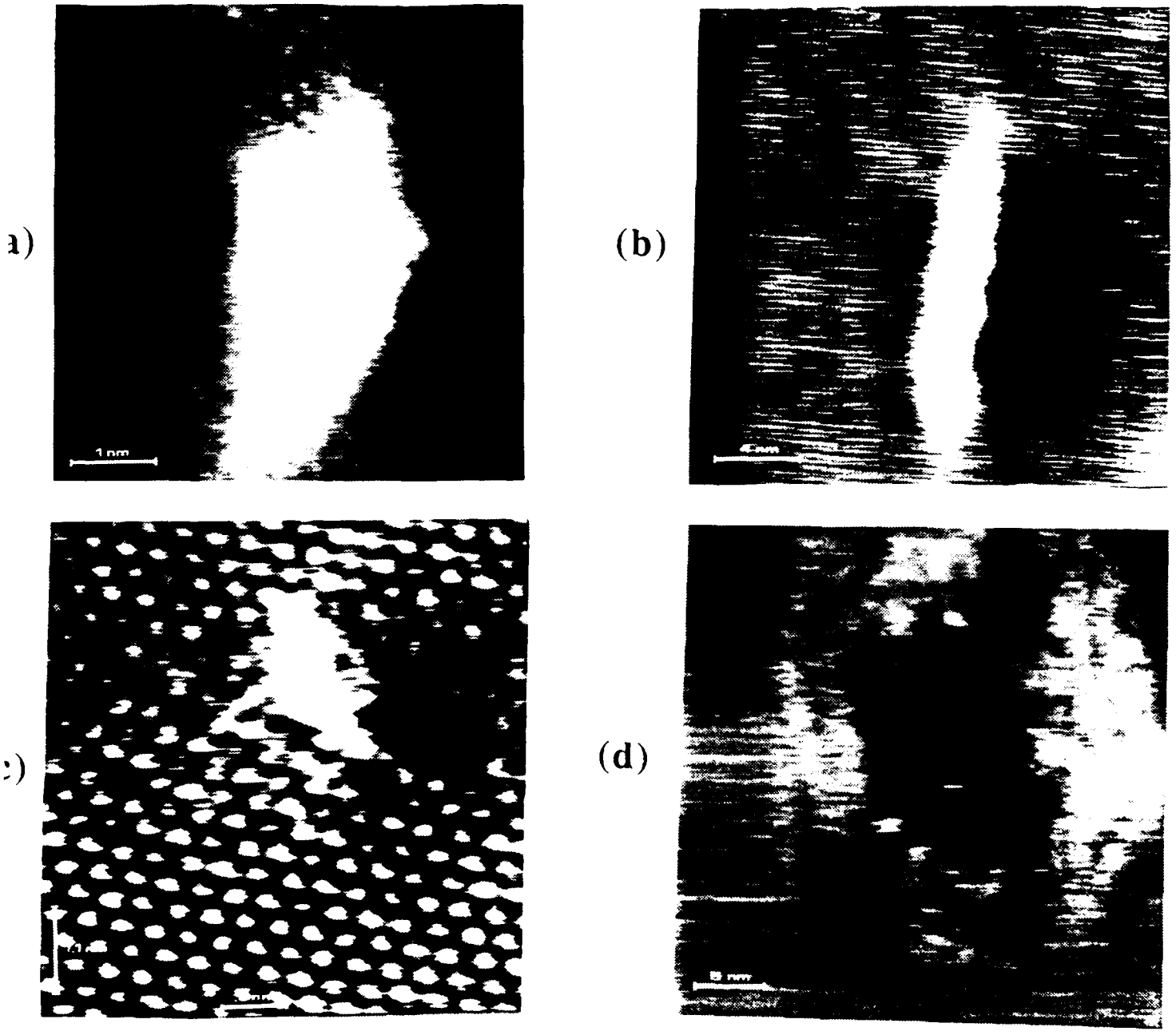


FIG. 4 Four views of the modification of a graphite surface

(a) Hillock formed in air with a pinning pulse of 4 V for 200 ns. (Pt/Ir tip)

(b) Hillock formed in decane with a pinning pulse of 4 V for 1 μs. (cold worked tungsten tip)

(c) Hillock formed in dimethyl phthalate with a pulse of 4 V for 400 ns. (etched, ion-milled tungsten tip)

(d) Depression in Highly Oriented Pyrolytic Graphite (HOPG) in decane with a pulse of 4.5 V for 200 ns. (Pt/Ir tip)
[From R. H. Bernhardt, G. C. McGonigal, R. Schneider, and D. J. Thomson, "Mechanisms for the deposition of nanometer-sized structures from organic fluids using the scanning tunneling microscope," *J. Vac. Sci. Technol. A* **8**, 667-671 (Jan/Feb 1990).]

For the first image, they pulsed the Pt/Ir tip to 4 volts in air for 0.2 microseconds and found a hillock on the substrate with a height of 5 Å, a length of 25 Å and a width of 17 Å. For the second image, Bernhardt used a tungsten tip immersed in decane ($C_{10}H_{22}$) and pulsed at 4 volts for 1 microsecond. The hillock measured 6.5 Å in height, 102 Å in length, and 17 Å in width. For the third image, a tungsten tip was immersed in dimethylphthalate and pulsed at 4 volts for 0.4 microseconds. The hillock was 8 Å in height, 21 Å in length, and 9 Å in width; similar in many respects to the hillock formed by Foster's group. There are "some striking similarities between the formation of hillocks in air and in liquids. In air, a likely mechanism for hillock formation is the transfer of material from tip to surface."

On several occasions the voltage pulses produced depressions in the graphite rather than a hillock. For the image of Fig. 4(d), the Pt/Ir tip, immersed in decane, was pulsed to 4 volts for 0.2 microseconds. This procedure produced a hole with a depth of 80 Å and a diameter of 260 Å.

These four examples illustrate the dilemma. The nature and source of the hillocks are undefined. If the hillocks were all made of *n*-alkane molecular clusters it would seem reasonable to see some evidence of molecular structure in the ordered molecular arrays - but so far the hillocks are featureless. There is no signature that can be used to identify the chemical nature of the attached species. The large depressions, or craters, are inconsistent with molecular pinning. More likely they are related to the enhanced etching of graphite.

The inconsistency in size, the change from hillocks to depressions, and the differing environments all contribute to a state of confusion in this field. Reactive processes which erode the graphite surface beneath the tip must be a factor in some of this. We will return to this subject in a later section.

IV. Liquid-Solid Interface -- Electrochemistry and Liquid Crystals

There is a substantial body of work concerning the operation of the STM in liquid environments. Surface reactions are observed in electrochemical cells with the tip and

sample immersed in various liquids; polar solvents,[25] non-polar solvents,[26] and conductive aqueous solutions.[27] In these solutions, where the current is carried by ions, a Heaviside double layer forms at the interface between the electrode and the liquid. Much of the potential drop is across the double layer. We direct our attention to the electrochemical reactions which occur in the region between the tip and sample.

Lin[28] and his colleagues in the laboratory of Bard in Texas, have demonstrated that the current from a scanning tip can control the etching rate associated with the light induced decomposition of III-V compounds. It is based on well-known work on photo-oxidation and the anisotropic etching of III-V semiconductors via the photoelectrochemical technique (PEC).[29-31] The incident light generates minority carriers in the depletion layer at the interface between the semiconductor and the electrolyte. Photons with energy greater than the band-gap participate in the generation of carriers and this permits one to use incoherent light. The lattice bonds, weakened in the presence of the minority carriers, are attacked by agents in the electrolyte.[32] The ratio of light to dark etch rates is greater than 100:1.

In the innovation introduced by Lin *et al.* the etching rate was enhanced by the current from the tip of the STM, modified to operate in an electrochemical cell. The tip, at the end of a wire sheathed in glass, was exposed to the electrolyte through a narrow opening in the glass tubing. It was spaced from the substrate by 1 micron and biased to -3 volts. The aqueous solution covering the sample consisted of 5 mM of NaOH and 1 mM of EDTA. When the sample was irradiated with a tungsten-halogen lamp they found that the "ratio of the local reaction rate across the substrate to that immediately under the tip was controlled by the current density distribution at the substrate surface." In the end, they were able to move the tip along a predetermined path and etch a line 0.3 microns in width on the GaAs surface.

Nagahara[33] and his colleagues working with Lindsay in Arizona, determined that they could use the photoelectrochemical technique in a buffered solution of $KAu(CN)_2$ to deposit gold atoms onto a substrate of p-GaAs. They worked with a Pt/Ir probe coated

with Apiezon wax[34] to minimize the faradaic leakage currents. There was a small opening at the tip to allow for the tunneling current. The tip was spaced approximately 100 Å from the substrate and biased at +2 volts with respect to the solution. The region was simultaneously irradiated with light.

Gold lines approximately 1000 Å in width were deposited on the substrate beneath the tip, as shown in Fig. 5. The light creates electron-hole pairs in this process and electrons move into the depletion layer to neutralize the gold ions in the solution. The neutral metal atoms are subsequently deposited on the substrate.

In this work, with the large gap between tip and sample. the line width is controlled by the lateral diffusion of the carriers, rather than the dimensions of the tip. It doesn't quite meet the spirit of the "local laboratory." In a second experiment, Nagahara and his colleagues[35] moved the tip within a few Angstroms of the sample and reproducibly etched lines in Si(100) with the STM tip. Light was excluded from the sample and the surface was covered with a dilute (0.05%) of HF solution. In this situation, where the Heaviside double layers at the tip and substrate overlap, the potential of the solution is not relevant. The process is controlled by the potential between tip and substrate. They biased the tip at +4 volts to etch the desired pattern. The minimum line width was 200 Å. The etching did not occur when they immersed the surface in other electrolytes, nor when the tip spacing was increased to 500 Å. They deduced that the etching was a field induced electrochemical process. A typical result is shown in Fig. 6.

V. Silicon

The group at Philips with van Loenen,[36] in their study of the surface of silicon, found that atoms could be easily removed from the Si(110) surface with a negative tip bias of 1.25 V. In their process, lateral scanning was interrupted and the *z*-piezo was extended to advance the tip toward the substrate by 20 Å. It was then retracted back to the original height. The time for this cycle was 8 ms. Subsequent imaging revealed that a hole was

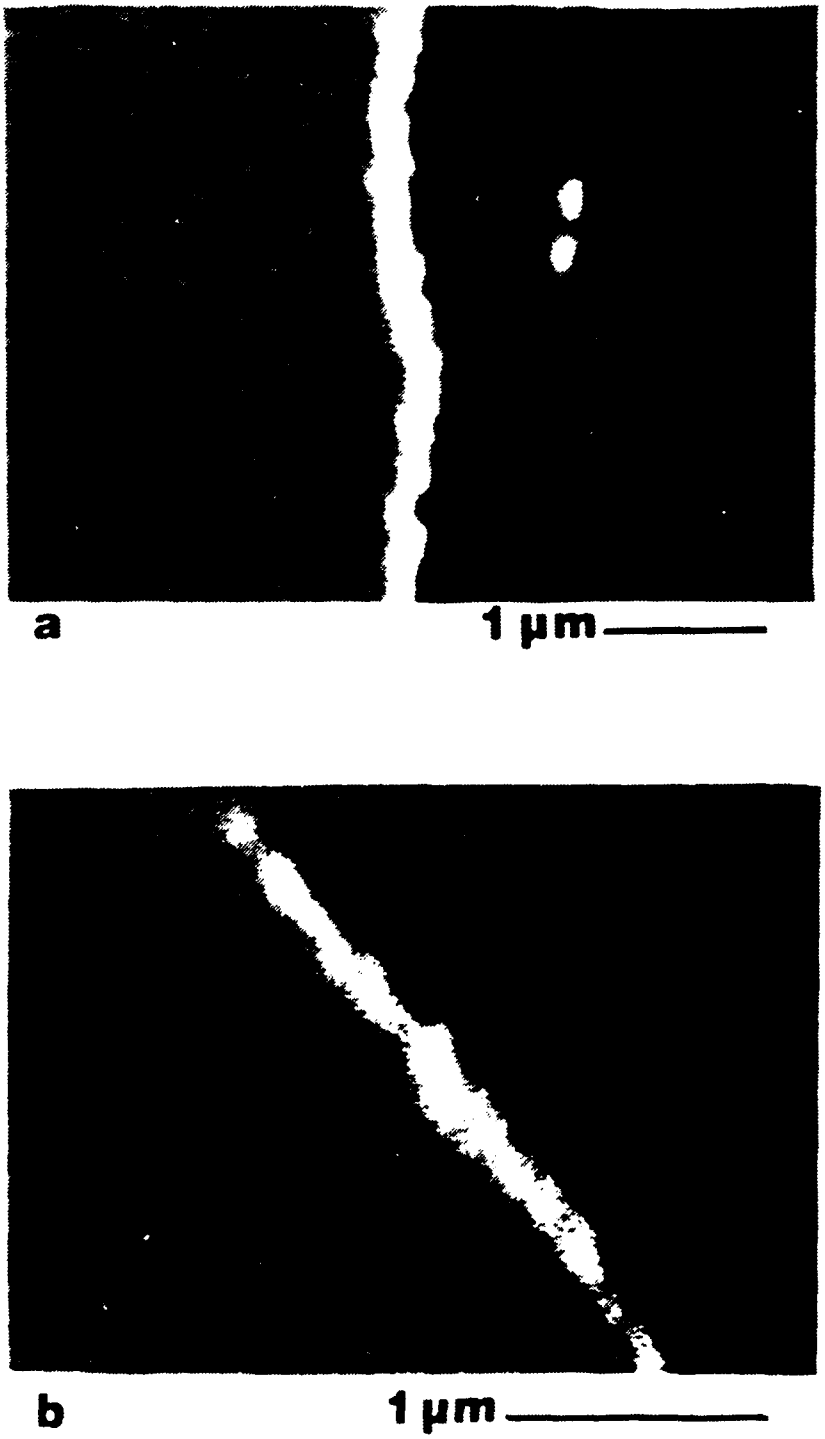
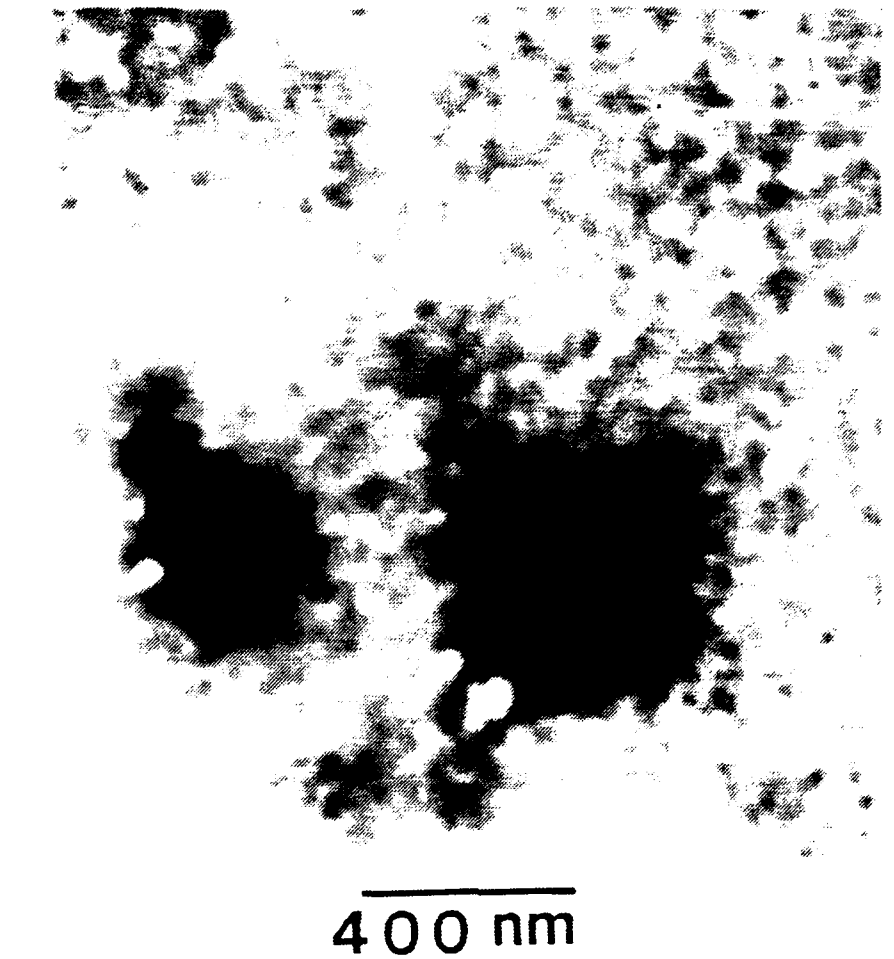


FIG. 5 Images from the STM of gold lines formed directly on p-type GaAs with the STM tip by photoelectrodeposition. The lines were written with a tip bias of +2 V with respect to the AG/AgCl electrode. [From L. A. Nagahara, T. Thundat, and S. M. Lindsay, "Nanolithography on semiconductor surfaces under solution using scanning tunneling microscopy," STM '90/NANO I, Baltimore, Md. (July 23-27 1990), to be published in *J. Vac. Sci. Technol. A.*]



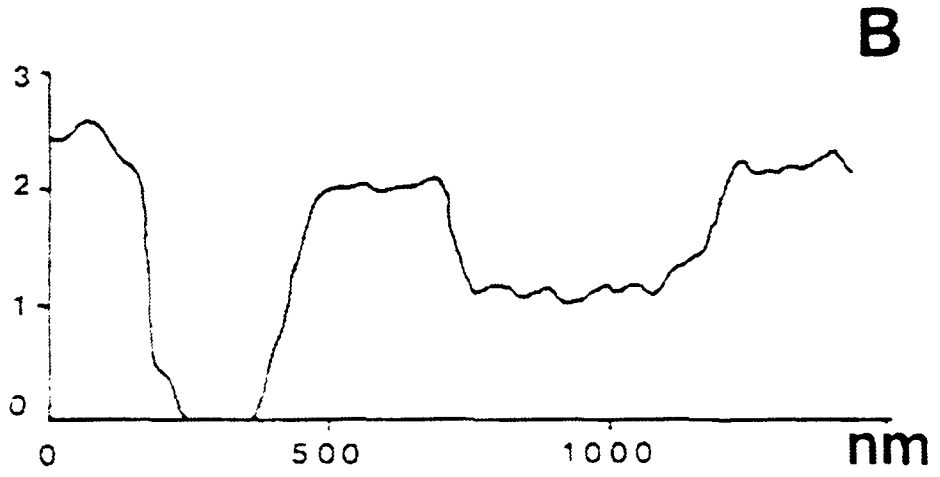


FIG. 6 (a) STM image of holes etched in silicon (100) in 0.05% HF solution. The tip was biased at 1.4 V with 1 nA of current

(b) Profile of the two etched pits showing the depth of the depression. [From L. A. Nagahara, T. Thundat, and S. M. Lindsay, "Nanolithography on semiconductor surfaces under solution using scanning tunneling microscopy," STM '90/NANO I, Baltimore, Md. (July 23-27 1990), to be published in *J. Vac. Sci. Technol. A.*]

formed in the substrate 20-50 Å in diameter and 7 Å in depth. The cycle was controlled and easily reproduced. They were able to "write" continuous lines on the silicon as narrow as 25 Å.

They examined the current dependence of this process and found that the holes still formed in the substrate when the tunneling current was turned off. The process was a function only of the *E*-field. The pattern of Fig. 7 is typical.

Iwatsuki *et al.*[37] at JOEL, in their study of silicon, connected the lateral motion of the tip to a "joy-stick" so as to move the tip under manual control. They found that silicon atoms on the Si(111) 7x7 surface could be continuously removed when the tip was moved across the surface with a bias of 10 volts. The "joy-stick" was used to 'write' lines in any desired pattern.

A group at Aarhus with Besenbacher and Mortensen,[38] have also used the technique of advancing the tip toward the substrate by extending the *z*-piezo while the tip is held stationary over a selected pixel. Their results are shown in Fig. 8.

In a similar way, Avouris[39] has written on Silicon (111) with the results shown in Fig. 9.

(a) H-Passivated Silicon

The surface of silicon is chemically modified with the diffusion of oxygen into the surface. It is known that the diffusion rate is increased when the surface is illuminated with electrons from an SEM.[40]

Dagata *et al.*[41] had this in mind when they speculated that diffusion of oxygen into a silicon surface might be enhanced with the *E*-field associated with the tip of the STM. Furthermore, if it could be done in air (or ambient oxygen), the vacuum environment of the SEM would not be required. As a first step, it would be necessary to passivate the surface. A system for doing this was disclosed several years ago in the work of Grunthaner and Grunthaner.[42] In that process the silicon wafer was cleaned and dipped in dilute hydrofluoric acid to remove the residual oxide. Predominantly, the dangling bonds of

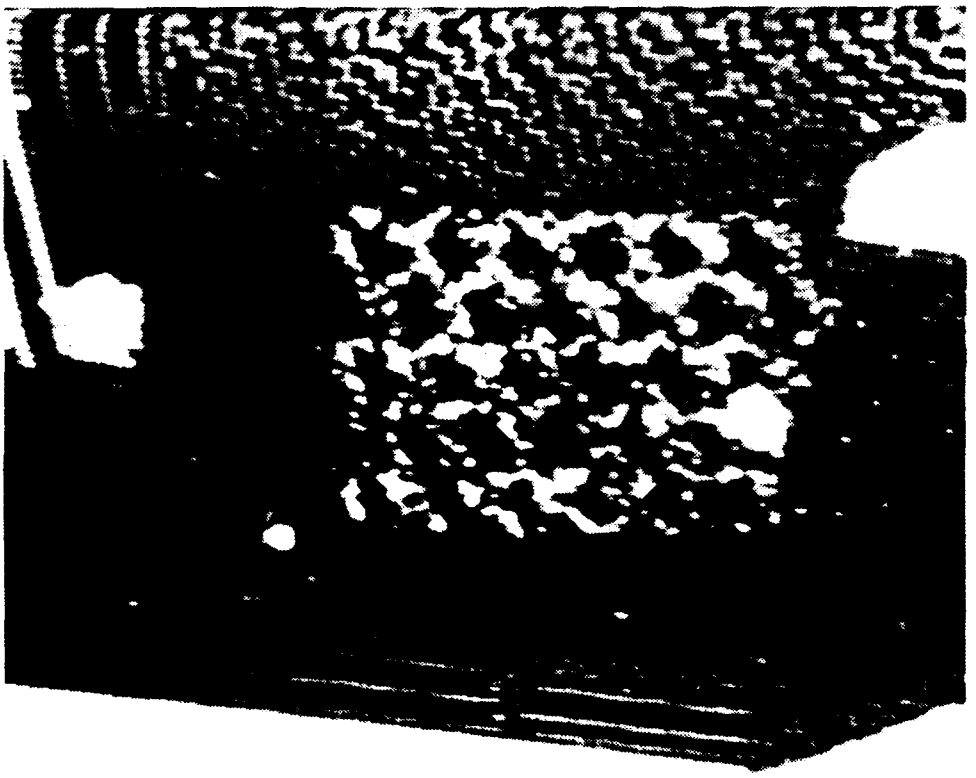


FIG. 7 Writing on silicon with the STM tip. [From E. J. van Loenen, D. Dijkkamp, A. J. Hoeven, J. M. Lenssinck, and J. Dieleman, "Direct writing in Si with a scanning tunneling microscope," *Appl. Phys. Lett.* **55**, 1312-1314 (25 September 1989).]

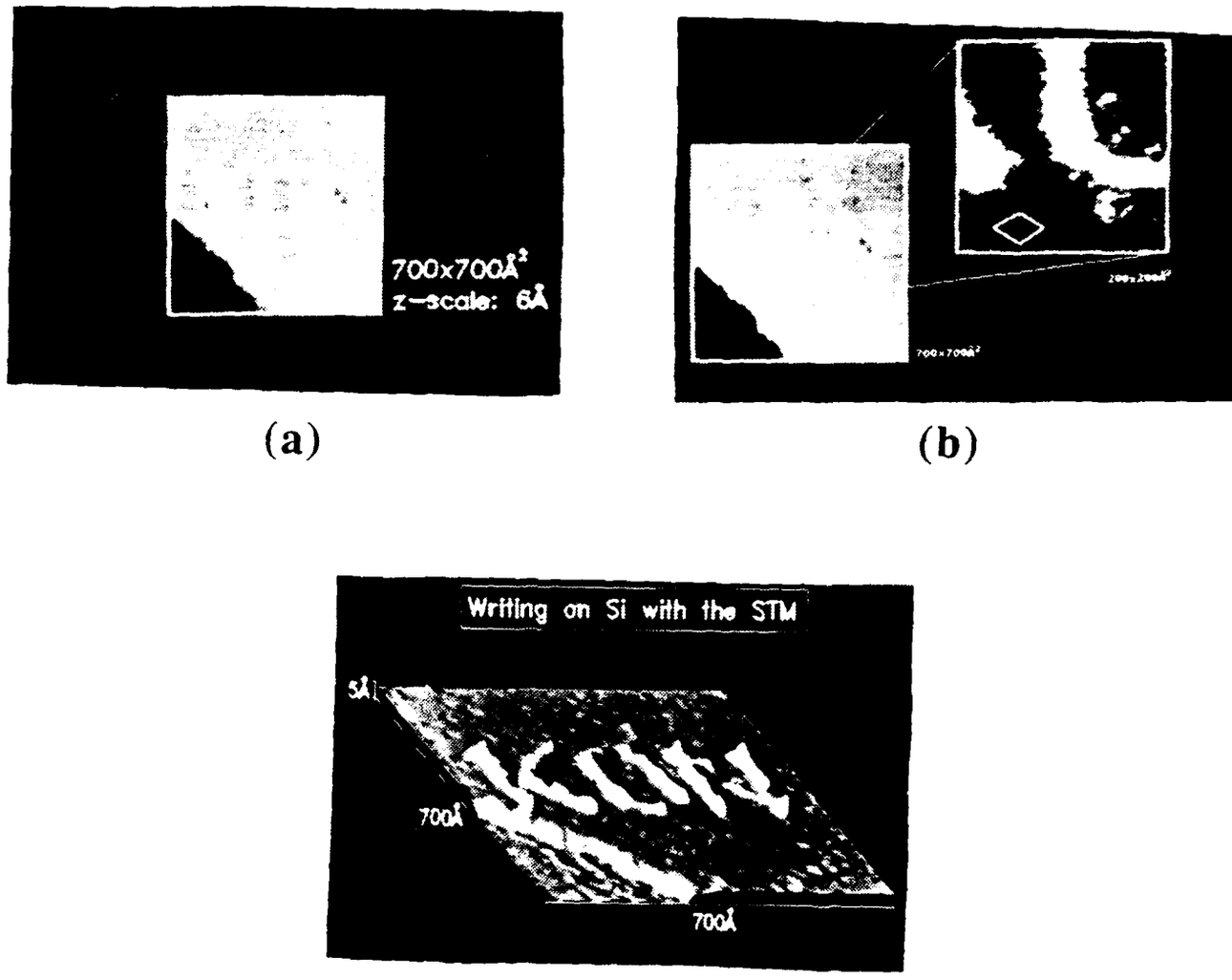


FIG. 8 Writing on silicon (111) 7x7 in honor of Prof. K. O. Nielsen. Tip biased at 2 V used in the manner described in the text. [Courtesy of K. Mortensen and F. Besenbacher, Aarhus University, Denmark.]

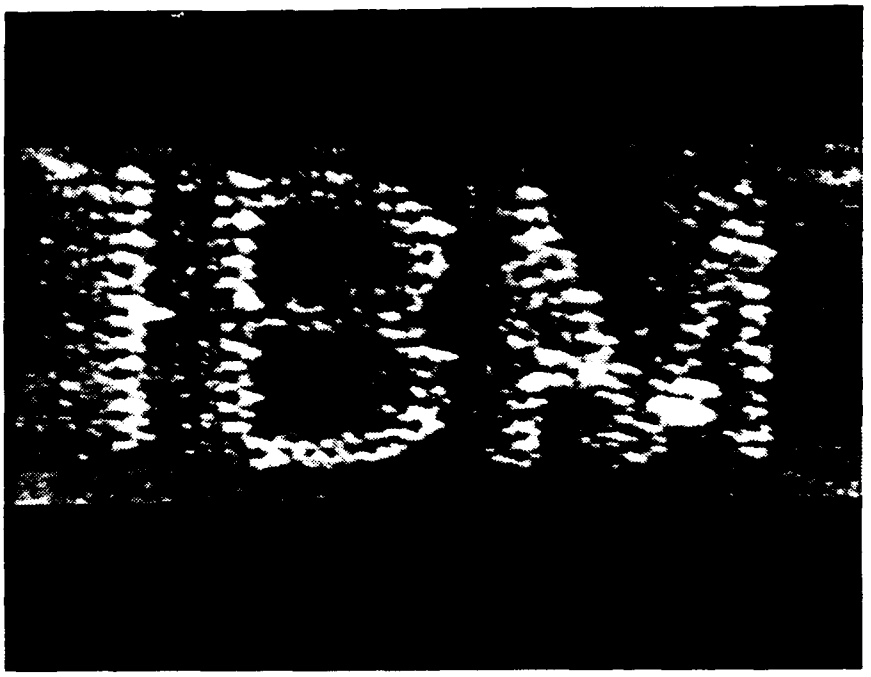


FIG. 9 Writing on silicon (111). [Courtesy of Ph. Avouris, IBM.]

silicon are terminated with hydrogen, rather than fluorine, and it is this termination that passivates the surface. The subject has been revisited by Fenner *et al.*[43] They state that "H termination reduces the rate of uptake of impurities, at low coverage, on the Si(100) surface by at least 10 orders of magnitude relative to the unterminated Si(100) surface." Surfaces passivated with this technique will survive in air for about 30 minutes before hydrocarbon contaminants clutter the surface and impede further processing. This is not a long interval of time, but it is most useful.

With this information in mind, the group with Dagata passivated silicon with hydrogen and scanned the tip over a preselected pattern. The tip voltage was fixed at 3.5 volts. When the oxygen molecule is dissociated, or ionized, by the intense *E*-field of the tip, the increased reactivity of the new species enhances the diffusion into the substrate. The process is labeled "diffusion enhanced oxidation."

In one instance they "wrote" a series of parallel lines - 200 nm in width, 3 microns in length, and spaced apart by 300 nm. The minimum line width was limited by the residual surface roughness of the silicon wafer. The surface texture of their wafers was 10-50 nm after passivation, but as they point out, this can be reduced with oxidation annealing prior to passivation.[44] A smoother surface would allow them to "write" finer lines. The scanned regions appeared as depressions in the STM images, but this is misleading. It was not topography, it was a change in the conductivity. When the conductivity of the surface region decreases the tip moves toward the sample to maintain a constant current. This movement appears as a depression in the image. The scanned area was examined in a SIMS apparatus and the examination revealed that the oxygen content was incorporated into the region to a depth of 1-20 nm.

In the final step, Dagata demonstrated that the patterned region was chemically distinct from the unmodified regions since the oxidized features could be selectively etched to a depth of 1 micron. The results are shown in Fig. 10.

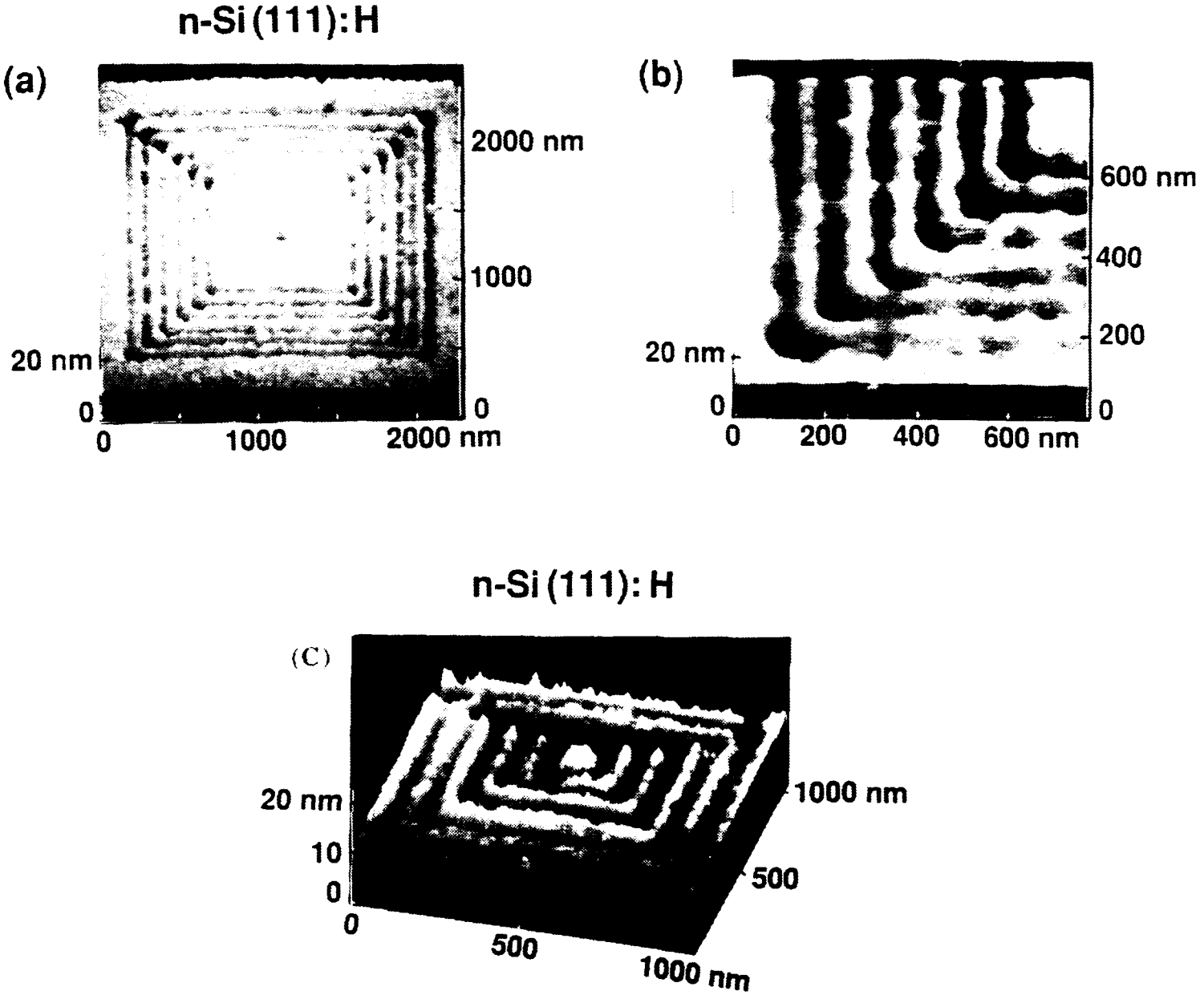


FIG. 10 The etched features on H-passivated, n-Si(111), $\rho = 10$ ohm-cm, by an STM operating in air

(a) Lines as written with a bias voltage of 3 V (tip positive)

(b) Detail of corner of the image of (a)

(c) Patterned features written on n-Si(111), with +3 V on the STM tip. [From J. A. Dagata, J. Schneir, H. H. Harary, J. Bennett, and W. Tseng, "Pattern generation on semiconductor surfaces by a scanning tunneling microscope operating in air," STM '90/NANO I, Baltimore, Md. (July 23-27 1990), to be published in *J. Vac. Sci. Technol. A.*]

VI. Phase Transitions

Phase transitions from the amorphous to crystalline state are interesting to many investigators. The lateral extent of the transition can be controlled if the material is heated above the transition temperature with a focused laser beam. The electron beam from the STM tip is a natural candidate for heating on the "local scale", but there is a problem. The temperature rise with a point source for heating is a function only of the thermal conductivity and the mean free path of the electrons. In crystalline materials, where the thermal conductivity is of the order of 100 W/mk and the mean free path is of the order of 10 nm, the temperature rise is only a fraction of a degree. However, in amorphous materials, where these values are reduced by a factor as large as 100, the heating produced by the tunneling electrons in the STM is substantial. We will discuss the results from the groups working in this area.

Staufer *et al.*[45] in Basel, examined the properties of metallic glasses. They found that this material can be smoothed to a surface roughness less than 1 Å by ion sputtering (Ar^+). A substrate with this degree of smoothness is suitable for nanometer-scale surface modification. With the tip in position over a selected point on the substrate, they increased the voltage to 2 volts (sample positive). This was followed by an increase in the current to 300 nA. The onset of instabilities in the current indicated that dramatic changes were taking place in the substrate material. Indeed, the evidence indicates that the temperature rise exceeds the melting temperature and a small pool of liquid formed under the tip. The molten glass was drawn toward the tip by the strong electrostatic forces to form a "Taylor cone." The current was lowered while the voltage was maintained at 2 volts. The cone froze into a hillock 300 Å in diameter and 150 Å in height. The size was dependent on the tip voltage - lower voltages produce smaller hillocks. It is easy to fabricate hillocks in the form of arrays, as shown in Fig. 11.

The group at Basel is proceeding to adapt their technique to media used in thermo-magnetic recording.[46] In that system, a ferromagnetic film is biased with a uniform

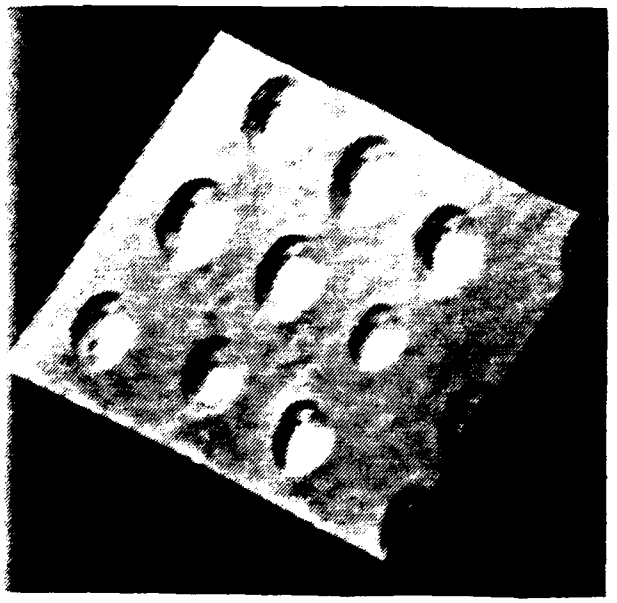


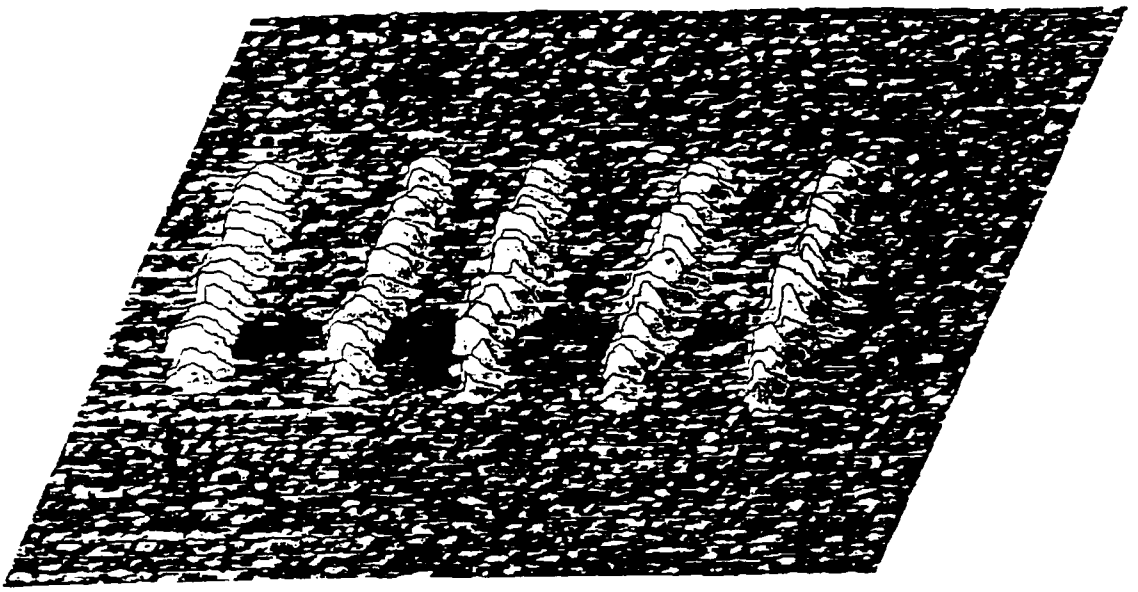
FIG. 11 STM image of cones written on the surface of $Rh_{25}Zr_{75}$. [From U. Staufer, L. Scandella, and R. Wiesendanger, "Direct writing of nanometer scale structures on glassy metals by the scanning tunneling microscope," *Z. Physik B - Condensed Matter*, **77**, 281-286 (1989).]

magnetic field and heated over a small "local" region to a temperature above the Curie temperature. The direction of the magnetization in the small heated region will change to match the direction of the bias field. The bias field is aligned with the bulk magnetization for writing, or against for erasing. Staufer *et al.* studied a Co-Tb alloy in the form of a metallic glass, $Co_{35}Tb_{65}$. A sample bias of 1.2 volts and a current of 50 nA was sufficient to melt the film and raise the "Taylor cone." They were able to "write" arrays of cones 50 Å in diameter and 5 Å in height in the presence of a magnetic biasing field. Information on the state of magnetization within the altered regions can be measured with magnetic tips, but this information is not yet available.

Hydrogenated amorphous silicon (a-Si:H) is another material with low thermal conductivity and short mean path for the electrons (10 Å). Jahanmir *et al.*[47] have studied a 200 Å film of amorphous silicon deposited on a silicon substrate. They pulsed the tip to 10 volts for 35 microseconds. The current during the pulse reached values as high as 100 microamps. They suggest that the increase in current elevates the temperature above the transition temperature and changes the film to the crystalline state. Lines were created by scanning the tip through distances as large as 1 micron. The lines were 150 Å in height and 1400 Å in width. The minimum size of these protrusions was limited by the inherent roughness of the surface.[48]

Hartmann,[49] in the group of Koch in Munich, has also studied the properties of amorphous silicon irradiated with the *e*-beam from an STM. They worked with *n*-type layers grown on *p*-type crystalline silicon substrates. The amorphous layers doped with hydrogen were 600 Å in thickness. They were able to modify the α:silicon layer with a negative bias of 10 volts on the tip. The modification, in the form of lines, is shown in Fig. 12(a) and (b). The linear features do not represent topography. It is a local change in conductivity induced by the high bias on the tip. The lines in Fig. 12 are 600 Å in width and 3500 Å in length. They were produced with a writing speed of 200 Å/sec.

(a)



(b)

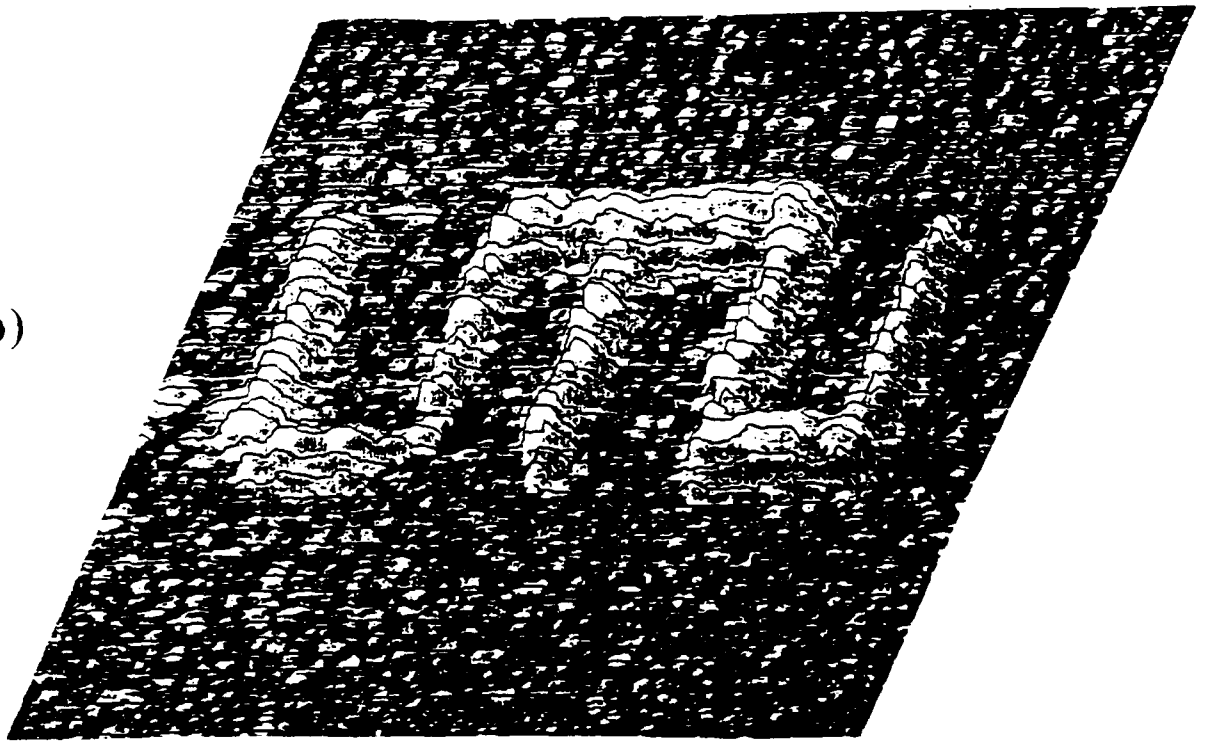


FIG. 12 (a) Hydrogenated amorphous n-type silicon (600 Å thick) deposited on a p-type silicon substrate. The linear features, 600 Å in width and 3500 Å in length, are written with a positive bias on the substrate of 10 volts. The images are recorded with a tip bias of 3-4 volts.

(b) Similar to (a) with the addition of the horizontal lines. In both (a) and (b) the linear features represent a change in the conductivity. The topography is not modified.
[Courtesy of E. Hartmann, G. Krötz, G. Müller, R. J. Behm, and F. Koch, University of Munich.]

Unfortunately, the written features are not stable. The relaxation time is measured in hours.

The mechanism is not yet understood. But the *pn*-junction at the interface between the *n*-type amorphous layer and the *p*-type silicon substrate must play a role. The phenomena does not occur with layers deposited on *n*-type substrates. It should, also, be kept in mind that the 10 volt bias is a very high value. It is in the range where atoms can be transferred between tip and substrate if the spacing is close.

Foster *et al.*[50] have considered the transition from the amorphous state to the crystalline state in a material such as GeTe. They propose to alter and convert discrete amorphous regions by heating to a temperature above the transition temperature with the STM. In the amorphous state the material is a semiconductor with a bandgap of 0.8 volts, whereas in the crystalline state it is nearly metallic with a bandgap of 0.1 volts. They estimate that the change from the amorphous state to the crystalline state can be induced in 50 nanoseconds with 8 volts on the tip. The reverse transition from crystalline to amorphous state might be induced with a similar voltage applied to the tip for 1 millisecond. The large change in the electrical properties should be easily detected with the STM in the imaging mode. These materials are highly reactive in air and a protective layer might be necessary to passivate the surface. Such a layer would impede the tunneling current and restrict the utility of this system.

VII. Conventional Methods for "Read-Write" Storage

There are two conventional systems for storage of digital information where the information can be "written" and "erased" with electrical signals. The first relies on the polarization of magnetization in small magnetic domains and the second relies on charge trapped in dielectric layers overlying a semiconducting substrate.

(a) Magnetic Recording with a Modified Tip in the STM

Moreland and Rice[51] have replaced the rigid tip of their STM with a compliant magnetized tunneling tip to study the field patterns on a magnetic hard disk. The magnetic probe was made from a nickel foil, 5 microns thick, shaped in triangular form. The apex of the triangle served as the tip. The probe was attached directly to the piezo-tube of the STM. The disk, taken from a computer drive, was aluminum with a magnetic coating of 1 micron film of CoCrTa. In one instance, the disk was overcoated with 1000 Å of gold.

In the writing cycle, the nickel tip was pressed against the substrate with a force that was estimated to be 2×10^{-9} N. The work was done at room temperature. They found that the magnetization in the film was altered over the full extent of the scanned area. They were able to "write" bits that measured 5000 Å across. The bits, shown in Fig. 13, could be imaged using the same tip with a resolution of 200 Å.

Their observation of recording and imaging magnetic regions in a controlled manner is an event that is central to the program of surface modification. Our understanding of the physical process underlying this phenomena will increase and it is probable that the bit size will shrink from the scale of microns to the scale of nanometers.

(b) Charge Storage - MNOS

Charge storage is the second area where the information can be written and erased in micron-scale structures. In 1981, Iwamura *et al.*[52] published a description of a system under the title "Rotating MNOS Disk Memory Device." It should be easy to adapt this to STM technology and create nanometer-scale structures. Their device was based on the Metal-Nitride-Oxide-Semiconductor technology used in conventional memory systems.

MNOS memory devices consist of a silicon substrate coated with a thin layer of oxide, about 20 Å in thickness. A second layer on silicon nitride with a thickness of 100 Å (or more) is placed on top of the oxide layer. A metal film is deposited over the nitride layer to complete the structure. In operation, a voltage on the metal film, positive with respect to the silicon, will cause electrons to tunnel from the silicon substrate through the

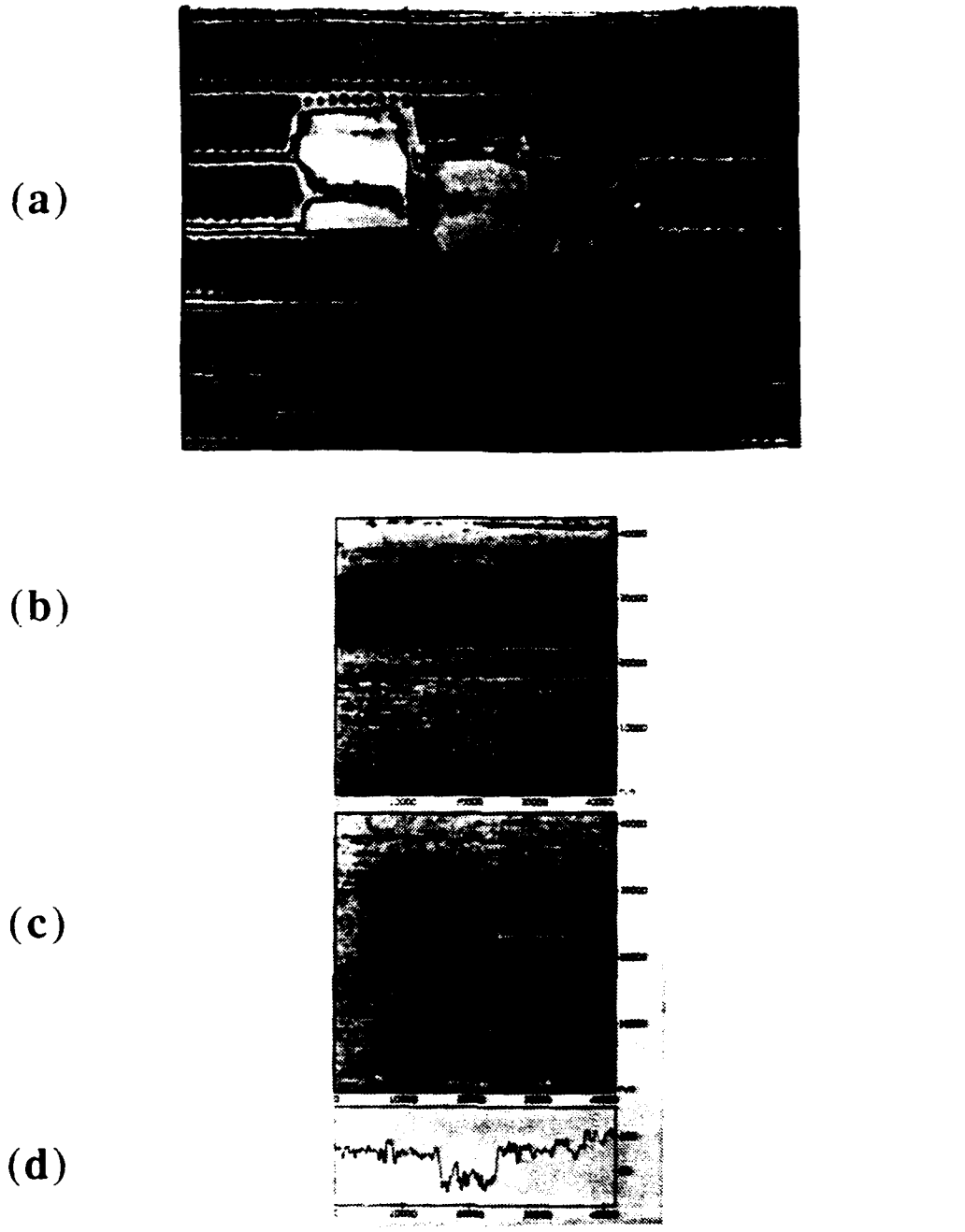


FIG. 13 Optical image of the surface of a hard disc decorated with ferrofluid showing the three squares with magnetization induced by the magnetic tip

(a) Optical image of the surface of a hard disk decorated with ferrofluid showing the three squares with magnetization induced by the magnetic tip

(b) The magnetic image of the hard disk before writing

(c) A magnetic square written with the magnetic tip

(d) The profile of the square of (b)
[From J. Moreland and P. Rice, "High-resolution, tunneling-stabilized magnetic imaging and recording," *Appl. Phys. Lett.* **57**, 310-312 (16 July 1990)

oxide layer into the nitride where it is trapped. The trapped charge creates a depletion layer at the silicon interface. The stored charge can be erased with a voltage pulse of the opposite polarity on the metal electrode.

The reliability for long-term storage in MNOS devices has been extensively studied. The process is well understood[53-56] and it gives us a firm foundation for future work with moving probes.

In the work reported by Iwamura, the deposited metal electrode was replaced with a movable gate electrode in the form of a rotating stylus 10 microns in diameter. The stylus moved in contact with the nitride layer - analogous to the motion of the flying head in magnetic hard disks. The stored information was read by sensing the depletion layer with the moving probe.

It is straightforward to adapt this technology to nanometer-scale structures by replacing the moving stylus with the narrow tip of the STM[57] to provide a new "read-write" system for high density storage.

VIII. Organometallic Deposition ala *e*-beam CVD

Deposition of atoms onto a substrate from a gas is known as chemical vapor deposition - CVD. When the gas molecules are irradiated with energetic particles they dissociate into volatile and non-volatile components. The volatile components move off and the non-volatile species deposit on the substrate. The energy for dissociation is furnished by various energetic beams that illuminate the region where the reaction takes place. Laser beams are used in laser-beam CVD,[58] and electron beams in *e*-beam CVD.[59] Metals, semiconductors and inorganic materials can be deposited with CVD. The feature size from laser CVD is limited to micron-scale structures, but *e*-beam CVD with the TEM, the SEM, or the STM can generate nanometer-scale features. We will introduce the discussion with the results from the TEM.

Matsui and Ichihashi[60] have used the "electron-beam-induced surface reaction" to dissociate WF_6 and deposit tungsten atoms onto a silicon substrate. They could watch the growth process *in situ* with their TEM. When the gas was irradiated with the electron beam, small tungsten clusters were formed. The initial clusters were quite mobile. A layer of tungsten was formed by the continuous coalescence of the clusters.

In this system for direct writing, the features are formed in place by deposition of metal atoms onto the substrate.

In a separate experiment, they fabricated the tungsten rod shown in Fig. 14. It has a diameter of 150 Å and a length of 1000 Å.

Matsui[61] also used a modified SEM to study electron-induced surface reactions as a method for etching micron-scale patterns in poly(methyl methacrylate) (PMMA). The lithography was carried out on the surface of PMMA in a vapor of ClF_3. In the absence of *e*-beam irradiation, the PMMA film was inert and immune to etching. In the presence of *e*-beam (10 keV, 100 pA) irradiation, the ClF_3 molecules dissociated and etched the PMMA to a depth proportional to the electron dose.

The technique for writing on PMMA with the SEM should lead to a similar system for lithography with the STM. The STM has not yet been used for etching PMMA, but it has been used to deposit metal atoms with *e*-beam CVD.

Electrons tunneling from a tungsten tip of the STM to a silicon substrate were used as the energetic source for molecular dissociation in the work of Silver *et al.*[62] Dimethyl cadmium (DMCd) molecules, with a dissociation energy of 3.14 eV, were adsorbed on a silicon substrate. The dissociation was then carried out with the STM operating at ll V with a current of 500 nA. They deposited cadmium on the substrate with a feature size as small as 200 Å.

McCord, Kern and Chang[63] operated an STM in the field emission mode (5-40 V) to deposit tungsten atoms on a silicon substrate with feature size as small as 100 Å. Two organometallic gases, tungsten hexacarbonyl and dimethyl-gold-acetylacetonate, were used

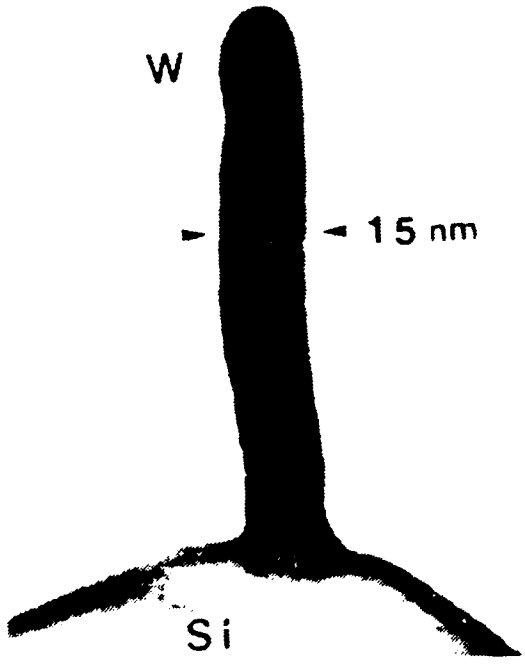


FIG. 14 A tungsten rod fabricated with a 120 keV electron beam via *e*-beam CVD. [From S. Matsui and K. Mori, "New selective deposition technology by electron beam induced surface reaction," *J. Vac. Sci. Technol. B* **4**, 299-304 (Jan/Feb 1986).]

as the vapor. These materials are easy to handle since they are solids that sublime at room temperature. In a vapor of $W(CO)_6$ with 16 mTorr of gas pressure, metallic lines were deposited on a silicon wafer with a central ridge 100 Å wide. The writing was done with a 30 V, 10 nA beam with the tip moving at 0.25 microns/sec.

In another instance, they wrote tungsten dots in a square array with a pitch of 0.25 microns. A single dot 300 Å in diameter was written in 0.5 seconds. A tungsten post standing 2800 Å high with a diameter of 250 Å was fabricated in 2 seconds.

This demonstration of tungsten lines, dots, and posts, will impact nanometer-scale devices where the dimensions of the structures are comparable to the wavelength of the electrons. If we ask about small ferromagnetic systems where the magnetic response is dominated by quantum mechanics, we turn to the work of Awschalom *et al.*[64] They report on a system with "...nanometer-scale magnets configured in regular arrays."

The nanometer-scale magnets were formed by dissociating pentacarbonyl [Fe(CO)] molecules with the STM. The magnetic structures were 250-1000 Å in height and 100-300 Å in diameter. The content of each cluster was estimated to be 60% FE and 40% Carbon. The magnetic particles, which are assumed to be amorphous, were grown under a pressure of 160 mTorr of Fe(CO) in about 100 msecs. The dimensions of the clusters of Fig. 15 are small compared to the thickness of the domain-wall in crystalline ferromagnets.

The important aspect of this work is that these small particles were fabricated in place on a special substrate which contained previously fabricated structures. The particles were placed on a sapphire substrate carrying the planar coils of a dc SQUID micro-susceptometer described by Awschalom[65] and shown in Fig. 16. The pick-up loop consisted of a pair of superconducting loops of lead, 25 microns on a side. One of the loops was covered with a gold film 800 Å thick. The magnetic particles were deposited in place on this loop with *e*-beam CVD, using the STM. They measured well-defined resonant peaks in the magnetic susceptibility at 500 Hz as the temperature was lowered below 0.2° K. This experiment is

STM direct deposition of magnetic particles from $Fe(CO)_5$

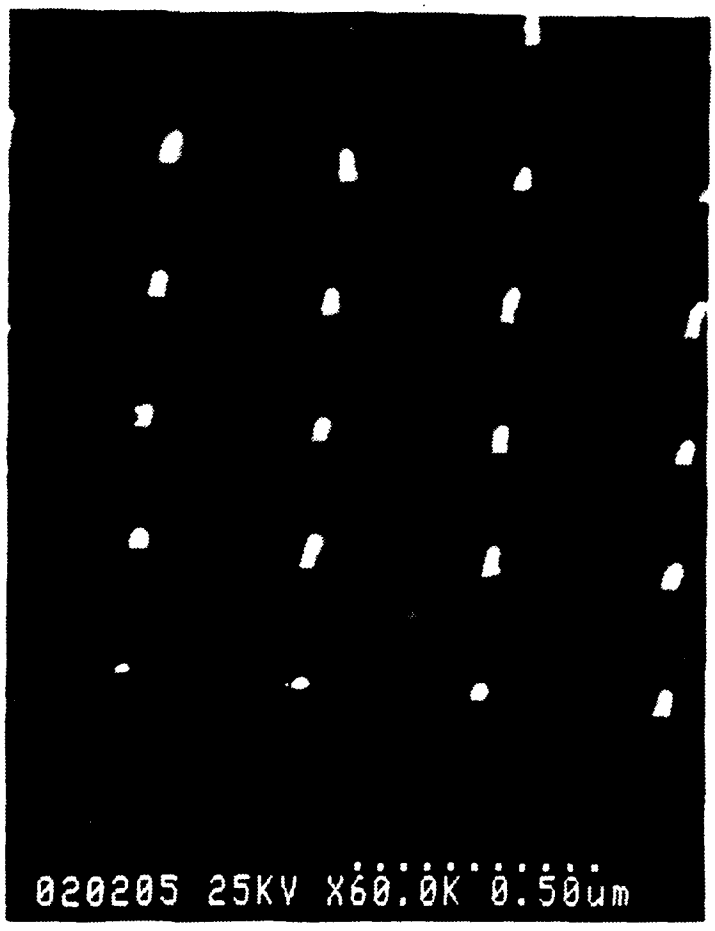


FIG. 15 Fe clusters formed by *e*-beam CVD with the STM. [Courtesy of M. A. McCord, IBM; also, D. D. Awschalom, M. A. McCord, and G. Grinstein, "Observation of macroscopic spin phenomena in nanometer-scale magnets," *Phys. Rev. Lett.* **65**, 783-786 (6 August 1990).]

Array of STM-deposited magnetic particles inside a planar SQUID pickup coil

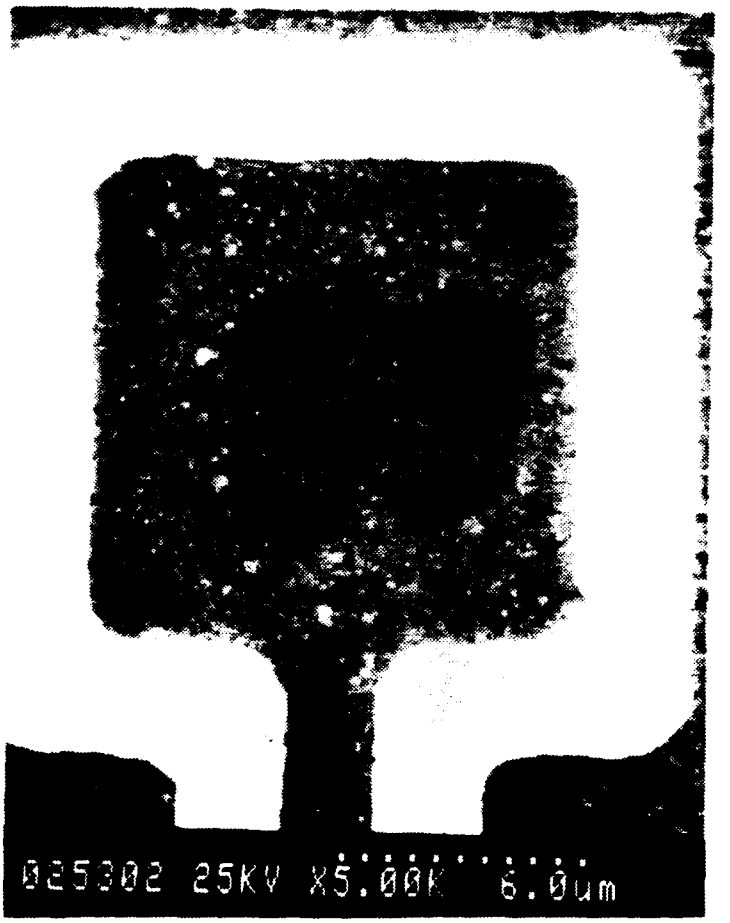


FIG. 16 A planar SQUID pick-up coil with the Fe clusters in place. [Courtesy of M. A. McCord, IBM; also, D. D. Awschalom, M. A. McCord, and G. Grinstein, "Observation of macroscopic spin phenomena in nanometer-scale magnets," *Phys. Rev. Lett.* **65**, 783-786 (6 August 1990).]

of great interest, even though their findings are not yet reconciled with the theoretical picture. It is a prime example of using the STM to fabricate an experimental device.

IX. Xenon on Nickel

A strategy for manipulating atoms on the surface is contained in the report from Eigler and Schweizer.[66] They propose to position xenon atoms by sliding them along a nickel surface with the tip of the STM. In a system cooled to 4° K they first adsorb a few xenon atoms on the nickel surface and then use the STM at 10 mV and 1 nA to image the atoms scattered randomly over the nickel surface. In the image, they select a given atom, position the tip over that atom and adjust the electronic system to increase the tunneling current. This advances the tip toward the atom and increases the force between the tip and the atom. They find that the force can be adjusted (by fine control of the spacing) to the point where the atom will slide and follow the tip as it is translated along the surface.

By sliding xenon atoms along a given row on the Ni(110) surface they form a well defined array of xenon atoms. The arrangement is stable with a spacing between xenon atoms of 5 Å. An example of a ring structure is shown in Fig. 17.

The fundamental character of these forces, the balance between the binding and translating forces, is independent of temperature. In the near future, we will discover a system where the atoms are assembled at room temperature by translation along the atomic rows of a smooth surface.

X. Graphite

The surface of graphite is easily modified with the STM when the tip, in close approach to the surface, is pulsed to a voltage above 4 volts. At first, this is quite surprising. Graphite is a layered structure where bonds between the carbon atoms in a given layer are very strong. The surface is inert and impervious. But, it should not be surprising, since the combustion and gasification of graphite proceeds via chemical erosion

FIG. 17 Atomic structure arranged by sliding xenon atoms on nickel with the tip of an STM. [Courtesy of D. M. Eigler, IBM; also, D. M. Eigler and E. K. Schweizer, "Positioning single atoms with a scanning tunneling microscope," *Nature*, **344**, 524-526 (5 April 1990).]

of the surface when the graphite is heated in a gaseous atmosphere. In the initial stages of combustion the surface erosion is similar in some respects to the surface modifications that are brought about in the STM. We will first review the combustion process and then review examples of electron enhanced etching.

In the process of chemical erosion, adsorbed particles, such as molecules and ions, react to form a new species with a lower binding energy. The new species desorb from the surface and leave a vacancy at the site of the erosion. The erosion rate increases when the energy of the adsorbed molecules is increased. The molecular energy is increased either by heating, or by illuminating the surface with secondary particles, such as electrons and photons.

In the combustion of graphite the material is heated in a gaseous atmosphere. In the initial stage, chemical erosion removes a monolayer of carbon over a small circular region 100 Å in diameter. The eroded regions appear as small etch pits with a depth of one atomic layer. A study of the characteristics of the etch pits leads to an understanding of the combustion process. More recently, it has been determined that etch pits of a similar nature can be created with a voltage pulse on the tip of an STM. Surface modification carried out in this way is reliable and well behaved. It is the point of interest for our report. Before proceeding, we will present background material on the combustion and erosion processes.

The reaction, central to processes of combustion and gasification of solid fuels, takes place when carbon is heated to 650° C in an atmosphere of gases such as H_2O, H_2, O_2, or CO_2. The reaction begins with the creation of the small pits. The pits are enlargements of vacancies, and other defects, where an edge is exposed in the uppermost layer. The reaction is initiated at the site of the sp^2 electrons. The rate of removal of atoms from an edge site in the layer plane is faster by ten orders of magnitude than the rate of removal of atoms from the surface of a perfect layer. Elementary rate constants, mechanisms for catalyzed reactions, and information on the earliest stages of combustion are revealed in the study of the etched pits.

The traditional method for studying etch pits is with the TEM using a technique labeled "etch-decoration transmission electron microscopy - ED-TEM." The technique was introduced in the late 50's by Hennig.[67] He found that gold particles deposited on carbon migrate to the edge of the pits and outline the circumference in a way that is easily recognized in the TEM. The shape and size of the pits are evident in the TEM images of Fig. 18. The depth is not available in the TEM images, it must be inferred from indirect evidence.

Yang[68] tells us that the technique for decorating with gold particles is "... difficult for beginners - in fact, temperamental..." This difficulty is circumvented if the STM is used to image the etch pits. Atomic detail with information on both shape and depth stand out in the STM images with high contrast; decoration with gold particles is unnecessary. Chang and Bard[69] have studied the etch pits formed by heating HOPG graphite to 650° C in an air furnace for several minutes. Their results are illustrated in Fig. 19. They propose the STM as a "powerful technique for studying the early stages of the gasification of graphite."

The chemical erosion, or deterioration, of graphite used as moderators in reactors has been dealt with in the work of Ashby *et al.*[70] They simulated the reactor environment by bombarding the graphite surface with atomic hydrogen. When they analyzed the volatile molecules in a mass spectrometer they found that methane (CH_4) was the major component in the desorbed species. They observed a "major reactivity enhancement" when the surface was simultaneously bombarded with electrons. The rate of methane production was increased by a factor of twenty.

Haasz[71] was able to confirm their results when he carried out similar experiments in a station with moderate vacuum, but he found no evidence for electron enhanced etching when he improved the vacuum with prolonged baking in a UHV station. Haasz found that in systems with a moderate vacuum methane molecules are adsorbed on the surfaces. He suggests that *e*-beam irradiation increases the methane production by releasing the adsorbed molecules.

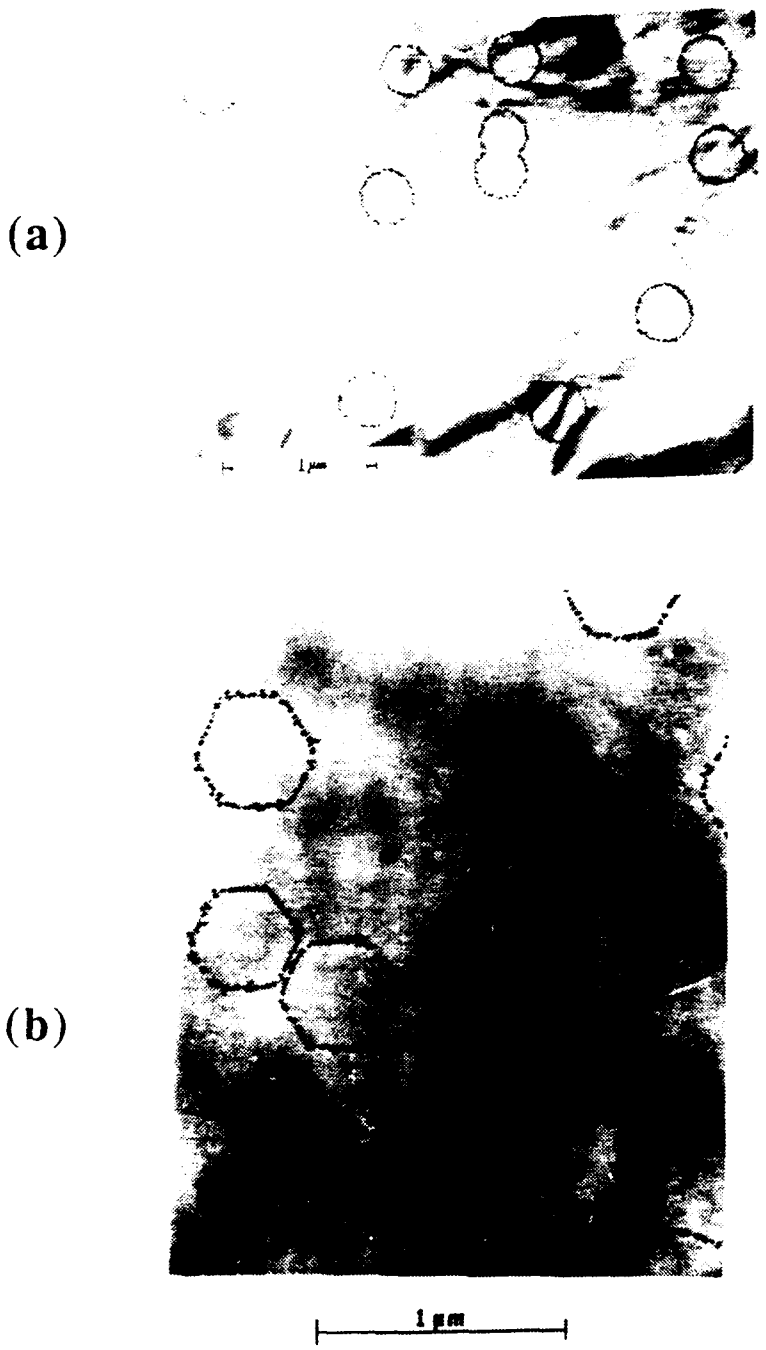
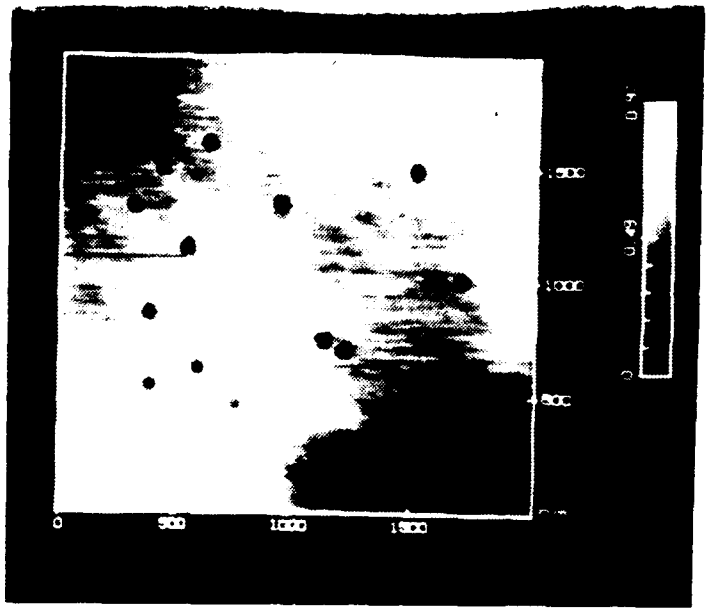


FIG. 18 (a) Transmission electron micrograph of the basal plane surface of graphite after oxidation for 25 min at 650° C with 0.2 atm 0_2 followed by gold decoration.

(b) TEM micrograph of gold-decorated monolayer etch pits on the basal plane formed by 23 torr H_20 (in 1 atm N_2) at 600° C for 14 h. [From R. T. Yang, "Etch-decoration electron microscopy studies of the gas-carbon reactions," in *Chemistry and Physics of Carbon*, vol. 19, pp. 163-210, P. A. Thrower, ed. Marcel Dekker, Inc. New York (1984).]

(a)



(b)

(c)

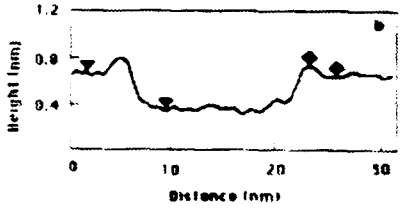


FIG. 19 (a) Image from the STM of etch pits in graphite after heating in air for several minutes at 650° C.

(b) An enlarged view of the etch pits in (a)

(c) A profile of the etch pit shown in (b)
[From H. Chang and A. J. Bard, "Formation of monolayer pits of controlled nanometer size on highly oriented pyrolytic graphite by gasification reactions as studied by scanning tunneling microscopy," *J. Am. Chem. Soc.* **112**, 4598-4599 (1990).]

Erosion of graphite at room temperature is, also, observed when the surface is bombarded with electrons. Enhanced etching with electrons is evident in the early work of Hennig and Monet.[72] They determined that single vacancies were created in perfect layers of graphite when the surface was irradiated with electrons (0.14 to 0.26 keV).

There is clear evidence[73] that "electron enhanced etching" is frequently encountered in the field of electron microscopy where carbon films are often used as supports for the specimens. It is common to find that these films are thinned in the region exposed to the electron beam. In one model for this process it is assumed that the water molecules remaining on the film are ionized with electron beams. The reactivity of the ionized species increases to the level where they can react with the carbon atoms to form CO. The volatile hydrocarbon removes carbon from the surface and creates the etched pits. Original work on this system is contained in the paper by Egerton and Rossouw.[74]

"Electron enhanced etching" of graphite has been reported by several groups working with the STM. Albrecht *et al.*[18] report that the graphite surface can be etched with a single pulse on the tip of the STM. Their STM was operating in air with high relative humidity. The pit, shown in Fig. 20, was formed by pulsing the tip to 5 volts for a few microseconds. The size and shape of the pits were identical to those observed by Chang and Bard in their thermal etching system. When the Albrecht group placed the samples in a vacuum station, thereby removing the H_2O molecules, they found that it was not possible to mark the graphite surface, regardless of the strength of the voltage pulse. In an atmosphere of N_2, the graphite was equally impervious to damage. However, the pits were readily formed with the voltage pulse when they reintroduced H_2O molecules. A typical pattern is shown in Fig. 21.

Terashima *et al.*[75] found similar results in their work on surface modification. Mizutani *et al.*[76] used this process to scribe structures with a special shape in the uppermost layer of graphite. They positioned the tip at successive points along the circumference of a circle 100 Å in diameter. At each point they pulsed the tip voltage to form small

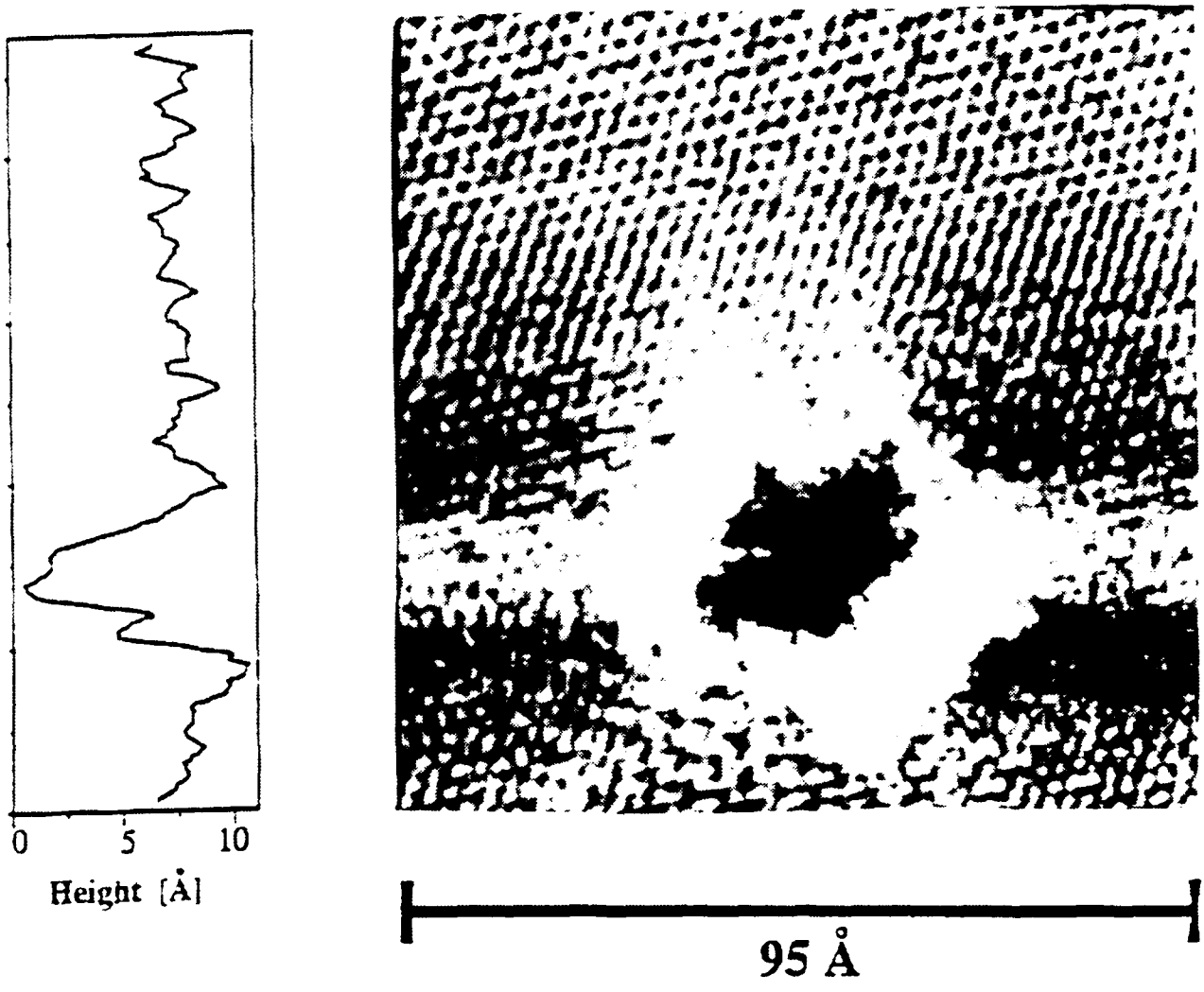


FIG. 20 Etch pits in graphite formed by pulsing the STM tip to 4 V for several μs in humid air. [From T. R. Albrecht, M. M. Dovek, M. D. Kirk, C. A. Lang, and C. F. Quate, "Nanometer-scale hole formation on graphite using a scanning tunneling microscope," *Appl. Phys. Lett.* **55**, 1727-1729 (23 October 1989).]

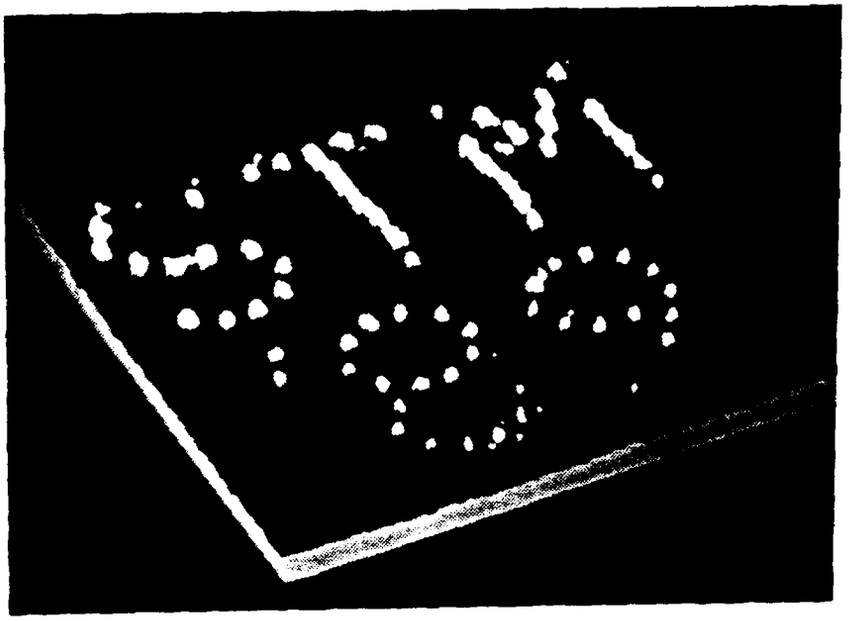


FIG. 21 Etch pits in graphite written with voltage pulses on the STM tip. [Courtesy of T. R. Albrecht and M. D. Kirk, Stanford University.]

overlapping pits as a circular ditch around the circumference. The monolayer disk inside the circle was exfoliated leaving the circular hole, conforming to the scribed outline, shown in Fig. 22.

Shen *et al.*[77] have observed similar pits when the tip of their STM was pulsed to 100 volts for 1 μs. The tip was spaced 100 Å from the substrate. It is likely that with this large voltage and large spacing, the molecules are ionized in the gap before they reach the substrate.

We mentioned in a previous section, the related experiment where Bernhardt[78] and Rabe[79] have successfully etched pits in graphite in ambient air.

More recent work has been reported by Penner *et al*[80] with an STM immersed in water. Domes, rather than pits, were formed on the graphite surface when the tip was pulsed to 4 volts for 20 μs. The domes were 7 Å in diameter and 1 Å high. The domes were converted to the monolayer pits 30-40 Å in diameter by positioning the tip over the dome and pulsing the tip to 200 mV. The moderate voltage for conversion suggests that the domes are metastable intermediates in the path to the formation of pits.

XI. Emission of Atoms -- Atomic Emission

A theme that occurs repeatedly in the work on surface modification is the creation of hillocks and craters. Several authors attributed their results to the transfer of material between the tip and substrate, but the mechanism for transfer was obscure. The situation remained cloudy until Mamin, Guethner and Rugar[81] did a careful study of atomic emission from a gold tip in close proximity to a gold substrate. They demonstrated that atoms can be transferred across this gap in a controlled fashion, consistently and reliably, with a threshold field of 0.1 V/Å. This is an order of magnitude lower than the field required to evaporate atoms from a tip in free space as in the Field-Ion Microscope (FIM).[82] This changes the character of the problem. Atomic emission should be considered in all of the events associated with the creation of hillocks and craters.

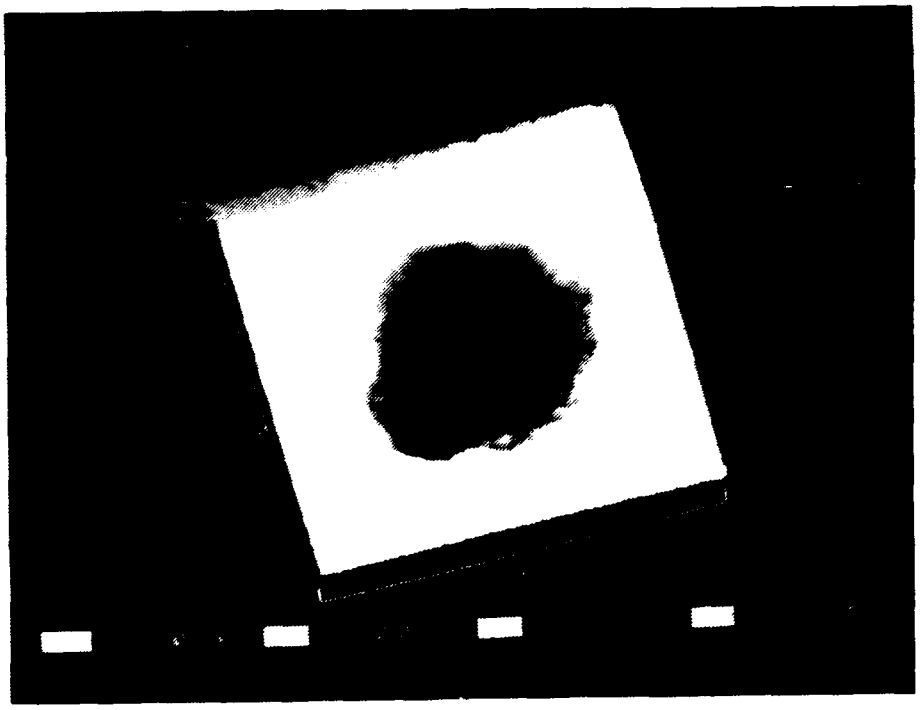


FIG. 22 A circular feature formed in graphite by fabricating overlapping etch pits around the circumference. [From W. Mizutani, J. Inukai, and M. Ono, "Making a monolayer hole in a graphite surface by means of a scanning tunneling microscope," *Jpn J. Appl. Phys.* **29**, L815-L817 (May 1990)

Before continuing with the Mamin-Guethner-Rugar report, we will discuss the various results on gold surfaces that followed the initial report from Berkeley.

(a) Gold -- Revisited

The tip of the STM has been used to alter the surface of gold and silver in several case studies. Gimzewski and Möller[83] examined the modification of thin silver films deposited on a Silicon (111) surface. They worked in UHV with a Platinum/Iridium tip biased in the positive direction with respect to the silver surface. They found that they could create hillocks 30-100 Å in diameter and 20 Å in height. The "... smaller structures tended to anneal out over a period of up to several minutes, ..." Different conditioning of the tips, "contaminated tips", would produce structures that appeared as indentations in the surface. Gimzewski and Moller suggested that "the tip itself may have contained a thin overlayer of silver previously deposited by field-emission cleaning. This may behave rather similar like a liquid-metal source reforming directly after contact .." They envisioned that the liquid metal formed a "neck of material which breaks, forming a local protrusion ..." when the tip was retracted.

Rabe and Bucholz[84] reported on similar events for the surface of silver films grown as epitaxial layers on cleaved mica.[85] They used a conventional STM with a Pt/Ir tip operating in ambient air. Holes appeared in the film when they pulsed the tip above 5 volts. On occasion, they observed mounds on the substrate when the *E*-field between tip and film approached 1 V/Å. Their results were attributed to field evaporation of atoms.

Jaklevic and Elie[86] studied the surface of a single crystal of gold. They deliberately advanced the tip toward the surface by increasing the voltage on the piezo element controlling the spacing. Surface craters were formed in this operation but they changed shape and filled within minutes. This was attributed to surface diffusion of mobile atoms. Jaklevic[87] reports that diffusion is very high on some surfaces with the cleanest surfaces exhibiting the highest diffusion rates. On other surfaces the diffusion rate was small, or non-existent.

Schneir *et al.*[88] took up the study with surfaces formed on the (111) facets of small gold balls. The balls were prepared by heating a gold wire to the melting temperature in the flame of an oxyacetylene torch, following a recipe described by Hsu and Cowley.[89] The facets, covered with fluorocarbon grease, were scanned with the STM tip immersed in the grease. They pulsed the tip voltage (biased negatively) to a value in excess of 3 volts to create both craters and mounds. The mounds were easily reproduced and in one instance the letter "T", as shown in Fig. 23, was written on the facet of their gold sample. The most reproducible mounds were generated "with the tips that had previously been pushed 100 nm into the gold surface with the *z*-axis piezoelectric element. (The tip was moved to a new region of the sample at least 20 microns from the site at which this procedure was performed.)" They found that the profiles flattened in a matter of hours with the gold diffusing outward from the mounds. Attempts to reproduce these results with the tip scanning in air were not successful.

Li *et al.*[90] report that the smooth (111) facet of a gold ball prepared by melting the end of a gold wire[91] can be "electroetched", a term they coined to describe the cratering of the surface when the STM tip voltage is suddenly increased to 2.7 volts. The work was done in air with a negative bias on the tungsten tip. The craters were 20-80 Å wide and 8-14 Å deep. They found no evidence of surface diffusion. The pattern shown in Fig. 24 is representative of what was done.

Emch *et al.*[92] studied the surface of a gold film epitaxially grown on mica.[93] They observed the formation of holes, and occasionally bumps, when the tip (biased positively) was pulsed to 3 volts for a time of 10-30 nanoseconds. The holes, 50-100 Å in diameter, were created on freshly prepared surfaces. On those surfaces where the diffusion rate was high, some of the step edges moved with a velocity of 5 Å/second.

The confusing aspect of this body of work is the different values for the diffusion rates. The time scales associated with a change in the features range from minutes to days and even months. The diffusion rates appear to depend on the nature of the atmosphere

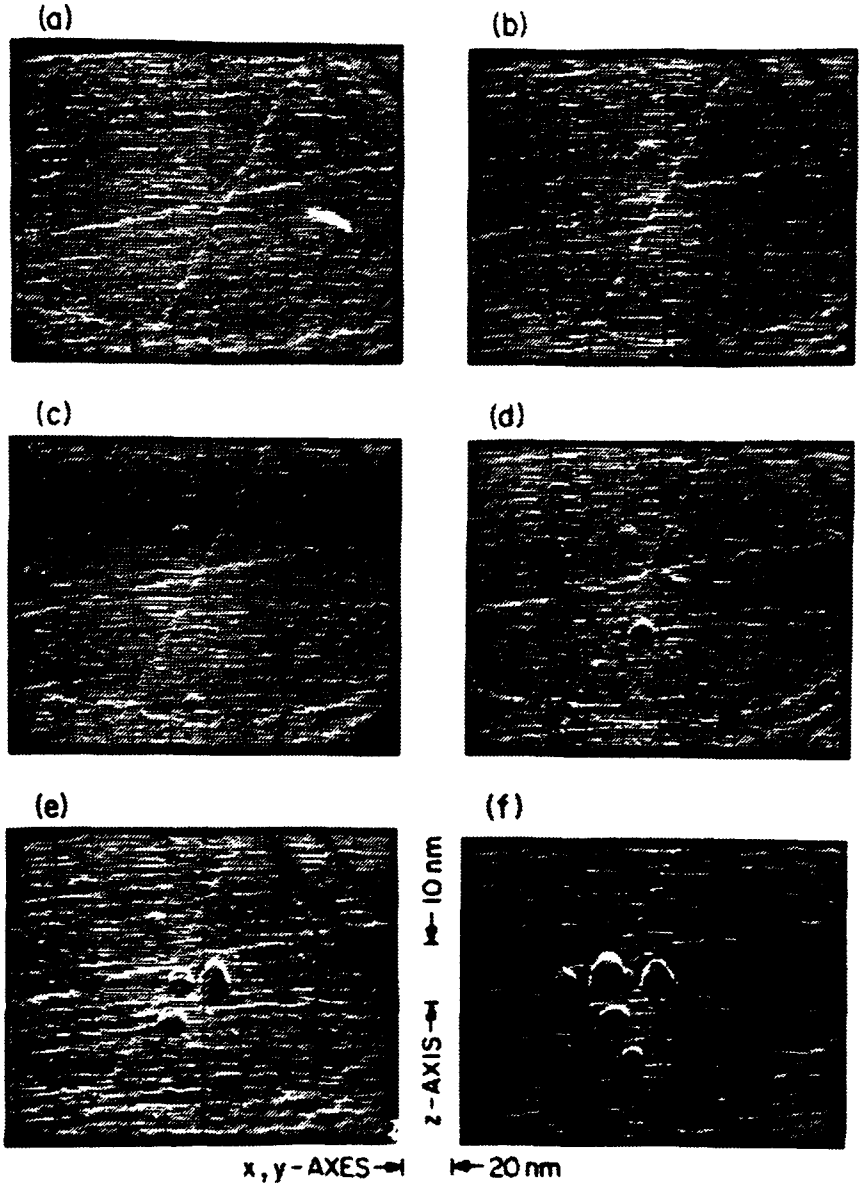


FIG. 23 A series of mounds written on gold (111) facet with 0.7 V on the tip of an STM with the surface covered with fluorocarbon grease. [From J. Schneir, R. Sonnenfeld, O. Marti, P. K. Hansma, J. E. Demuth, and R. J. Hamers, "Tunneling microscopy, lithography, and surface diffusion on an easily prepared, atomically flat gold surface," *J. Appl. Phys.* **63**, 717-721 (1988).]

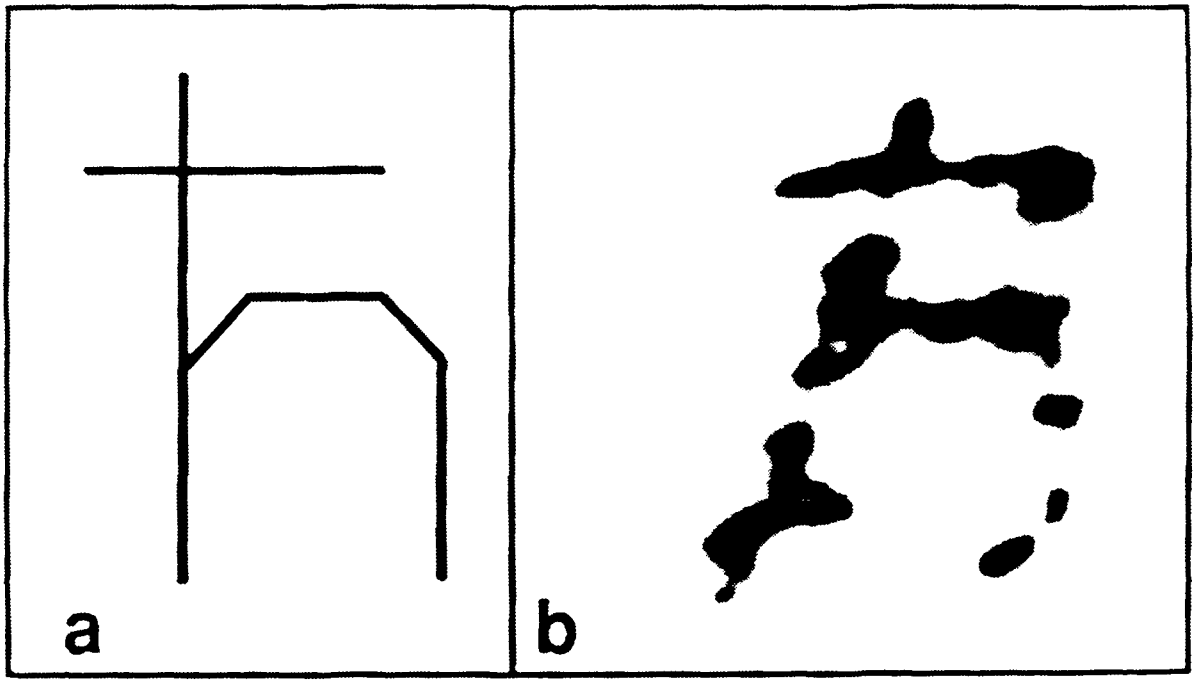


FIG. 24 (a) A computer generated template of the symbol h-bar. The template is comprised of 201 coordinate points out of a possible 10,000. At each specified coordinate point, a voltage pulse is applied to a tungsten tip executing an STM scan.

(b) A subsequent scan of the STM tip over the same region reveals the STM image which is the h-bar symbol electroetched into a flat Au substrate. The h-bar symbol is ~ 65 nm high, ~ 40 nm wide, and ~ 2 nm deep.
[Courtesy of R. Reifenberger, Purdue University; also, Y. Z. Li, L. Vazquez, R. Piner, R. P. Andres, and R. Reifenberger, "Writing nanometer-scale symbols in gold using the scanning tunneling microscope," *Appl. Phys. Lett.* 54, 1424-1426 (10 April 1989).]

during evaporation of the gold atoms. Jaklevic tells us that ".... a third element must be involved."[94]

One informative study that bears on the problem of diffusion rates was carried out by Francois *et al.*[95] Their evidence proves that the character of deposited gold films is dependent on the environment during evaporation. Francois studied the deposition of gold clusters onto a silicon substrate from an LMIS. (LMIS is an ion source described in the next section.) They used a strong magnetic field between source and substrate to spatially separate species with different charge to mass ratios. They found subtle differences in films deposited in the presence of energetic ions and those deposited in the absence of energetic ions. If energetic ions were present the film morphology showed a granular character with good integrity and strong adhesion to the substrate. It was inferred from the shape of the balls on the surface that there was little surface diffusion. The shape of the balls reproduced the shape of the spherical droplets emanating from the LMIS source. When the energetic ions were removed by deflection in the magnetic field the film morphology changed, the film integrity was lost and the adhesion to the substrate was degraded.

The work of Francois is enlightening for it tells us that the surface of gold is ubiquitous. The stability of nanostructures - however they are created - depends on the environment during creation. With this evidence in mind, it should not be surprising that gold hillocks deposited from the STM tip exhibit different behavior when they are formed in UHV, in air, and in other environments. The process must involve the transfer of material between tip and sample but the mechanism for transfer is unclear. The situation was clarified in the work of Mamin and Rugar, but before we inquire into that we want to discuss two classical systems for extracting atoms from condensed systems: the Liquid Metal Ion Source (LMIS), with a threshold field of 0.1 V/Å, and the Atom-Probe, with a threshold field of 1 V/Å.

(b) Emission from LMIS

The Liquid Metal Ion Source (LMIS) is a prolific source of ions used for applications in ion beam microlithography,[96] and micromachining.[97] The conventional LMIS employs a heated tungsten needle with a shank 2 mm in diameter tapered to an apex with a radius of 2 microns. The shank is immersed in liquid metal and capillary action coats the apex with a thin layer of the molten metal. The liquid metal, wetting the needle, forms into a cone when a high voltage (10 kV) is applied.[98] It is known from the work of Taylor[99] that a liquid surface under the influence of a strong electric field will form into a stable cone where the stress of the electric field tending to stretch and elongate the cone is balanced by the surface tension acting to contract the cone. In "Taylor cones" with a half-angle of 49.3 degrees these two counter forces balance each other over the entire surface. Gallium, with a surface tension of 0.72 joules/mtr^2, and melting temperature near 30° C, is the preferred metal, but gold with a surface tension of 1.1 joules/mtr^2, and a melting temperature near 1000° C, has been employed in many instances. Other metals using LMIS[100] include: Ga, In, Al, Au, Ag, AuSi, Pd_4B_6, and Pd_2As.

Copious amounts of ions are emitted from the liquid "Taylor cones" when the field reaches the threshold. The threshold field for atomic evaporation is above 1 V/Å, but the field applied to the tip is much less (0.1 V/Å). The reduction in applied field comes about in the following way. The maximum field at the apex of the cone produces a finger-like protrusion from the apex with a small radius of curvature and this protrusion increases the field strength to the threshold for atomic evaporation.[101]

The LMIS is a unique ion source with the following properties: (1) high angular beam intensities, (2) moderate energy spreads, (3) small source size, and (4) high stability with little movement of the cone over long periods. The stability makes it feasible to use focused beams from the LMIS for the repair of microcircuits. These attributes and applications are discussed by Swanson *et al.*[102] The characteristics of gold ions from an LMIS are discussed by Wagner and Hall.[103]

In variation of the standard version of the LMIS, Bell *et al.*[104] turned to a configuration similar to the STM. They found stable emission with low voltages using gallium coated tungsten needles when the spacing between the apex of the cone and the substrate was reduced to a small value. Their experiment was complicated by the extension of the liquid surface when the cone was formed. The extension can be as large as 1 micron. In spite of this, Bell and his colleagues were able to place the LMIS source 1000 Å from the substrate and deposit lines with their tips biased at 100 volts. These lines, 1000 Å in width, stood as a prime achievement until Mamin and Rugar demonstrated that atoms could be directly emitted from the solid gold tip. In this circumstance, where there is no molten metal at the tip, it is an easy matter to place the tip in close proximity to the surface.

(c) Emission from Atom-Probes

The Field-Ion Microscope (FIM)[105] which provides a view of individual atoms on metal surfaces can be combined with a mass spectrometer. This combination is used to identify the chemical species of evaporated atoms. It is known as the Atom-Probe FIM.[106,107]

The process for removing atoms from the metal tip of the FIM is known as field evaporation,[108] or field desorption.[109,110] In this process, a 3 kV voltage pulse is applied to the FIM for several nanoseconds. This pulse generates a field in excess of 1 V/Å at the surface of the metal tip.[111] Several monolayers can be removed in a few nanoseconds.[112] Multiple charged ions, neutral atoms, and atomic clusters, are frequently observed in the emitted beams.

It is a simple and surprisingly efficient process for removing atoms from the top layer from a solid metal tip.

(d) Gold Surfaces -- Final Results

We return to our final topic - the demonstration by Mamin, Guethner and Rugar of field evaporation from solid metal tips.

Their advance over previous work was the discovery that the barrier for field evaporation is reduced when a conducting surface is in close proximity to the tip. The barrier is lowered to the point where they get atomic emission with a threshold voltage of 3-5 volts between tip and sample.

The evidence for lowering of the barrier comes from the experimental measurements. The measured threshold for a tip in close proximity to a metal surface is near 0.1 V/Å compared to a value in excess of 1 V/Å for a tip in free space.

The model for field desorption from a tip in free space has been worked out by Müller *et al.*[82] Mamin proposes that the height of the barrier in Müller's model is reduced by the overlap of the atomic potentials when a metal surface is brought close to the tip. The reduction in barrier height is significant for atomic emission is achieved with modest voltages.

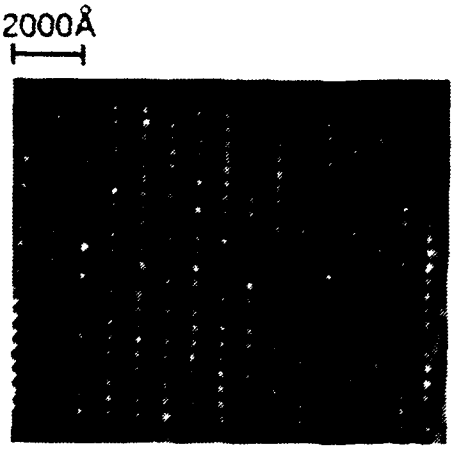
Mamin *et al.*[113] used a gold tip formed at the end of a wire 250 microns in diameter electrochemically etched to a radius less than 1 micron. A single voltage pulse of 3.6 volts (sample positive with respect to the tip), 600 nanoseconds in length was sufficient to evaporate atoms and form mounds on the substrate. The procedure can be repeated without end. The tips appear to be self-annealing. This suggests that the gold atoms are drawn from the shank toward the tip to replenish the evaporated atoms. The mounds are 80-100 Å across at the base and 20-30 Å in height. The process is fast and reproducible. Mounds can be written with pulses as short as 10 nanoseconds. This is consistent with the data quoted earlier when 10 monolayers are evaporated in a few nanoseconds from the Atom-Probe. Furthermore, there is no diffusion when the gold atoms are deposited in air.

The printed dots are remarkably stable. The stability is illustrated in Fig. 25. The pattern of dots remains in place after many hours at elevated temperatures.

In closing, we present the logo of Fig. 26. It is a representative sample of the level of maturity that now exists in this field.

(a)

Ultra-High Density Storage with the STM



Au(111) surface
Etched Au tip

Pulse parameters -4.4 V
300 nsec

Density ~10^{12} bits/in^2

(b)

Direct Deposition From A Gold STM Tip

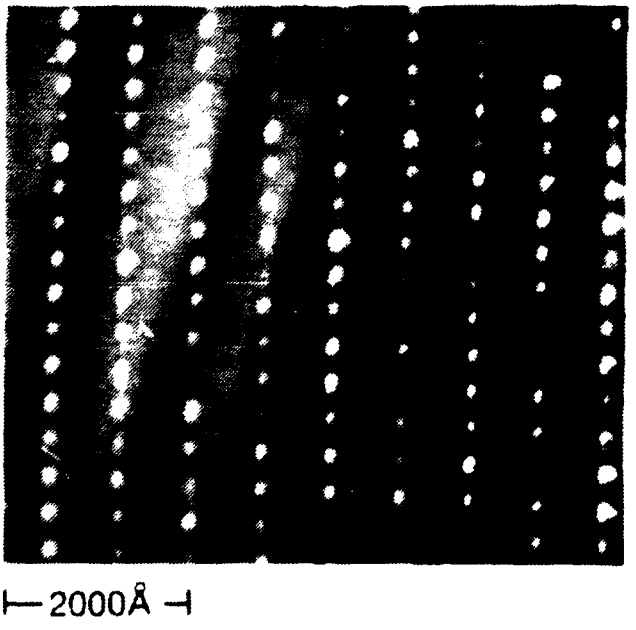


FIG. 25 Hillocks on gold formed with a negative pulse on the STM tip. The mounds are stable over periods in excess of 15 days. [From H. J. Mamin, S. Chiang, H. Birk, P. H. Guethner, and D. Rugar, "Gold deposition from a scanning tunneling microscope tip," STM '90/NANO I, Baltimore, Md. (July 23-27 1990), to be published in *J. Vac. Sci. Technol. A.*]

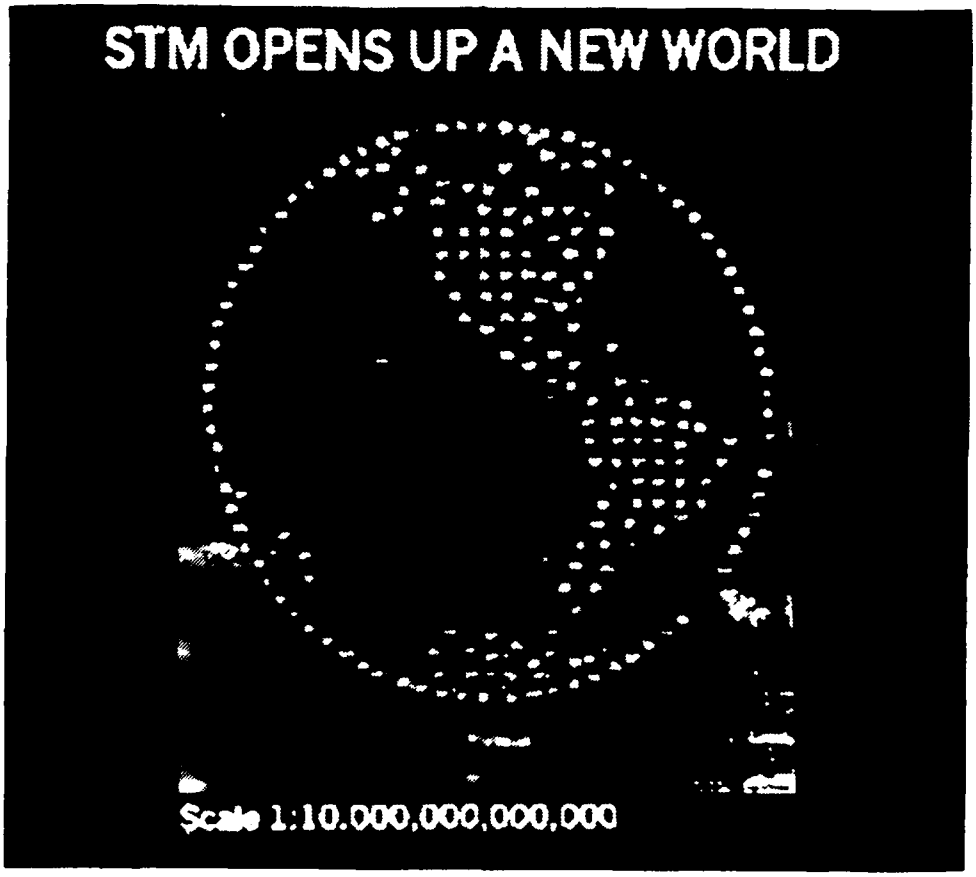


FIG. 26 Logo written on a smooth gold surface with atoms emitted from a gold tip of an STM operating in air. [Courtesy of H. J. Mamin, IBM.]

The work of Mamin, Guethner and Rugar has clarified our thinking and resolved a number of conflicting issues. With gold tips and gold substrates they have given us a clear demonstration of the transfer of atoms from the tip to substrate, or from the substrate to the tip. This striking advance in surface modification opens a path for fabricating nano-scale structures.

Acknowledgement

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References

1. G. Binnig and H. Rohrer, "Scanning tunneling microscopy," *IBM J. Res. Develop.* **30**, 355-369 (July 1986).
2. C. F. Quate, "Surface modification with the STM and the AFM," in *Scanning Tunneling Microscopy and Related Methods*, pp. 281-297, R. J. Behm, N. Garcia and H. Rohrer, eds., Series E: Applied Sciences, Vol. 184, Kluwer Academic Publishers, Dordrecht, The Netherlands (1990).
3. G. M. Shedd and P. E. Russell, "The scanning tunneling microscope as a tool for nanofabrication," *Nanotechnology*, **1**, 67-80 (1990).
4. D. W. Abraham, H. J. Mamin, E. Ganz, and J. Clarke, "Surface modification with the scanning tunneling microscope," *IBM J. Res. Develop.* **30,** 492-499 (September 1986).
5. R. S. Becker, J. A. Golovchenko, and B. S. Swartzentruber, "Atomic-scale surface modifications using a tunnelling microscope," *Nature*, **325**, 419-421 (29 January 1987).
6. M. Ringger, H. R. Hidber, R. Schlögl, P. Oelhafen, and H. -J. Güntherodt, "Nanometer lithography with the scanning tunneling microscope," *Appl. Phys. Lett.* **46**, 832-834 (1 May 1985).
7. M. A. McCord and R. F. W. Pease, "Lithography with the scanning tunneling microscope," *J. Vac. Sci. Technol. B* **4**, 86-88 (Jan/Feb 1986).
8. R. L. Stewart, "Insulating films formed under electron and ion bombardment," *Phys. Rev.* **45**, 488-490 (April 1, 1934).
9. A. N. Broers, W. W. Molzen, J. J. Cuomo, and N. D. Wittels, "Electron-beam fabrication of 80-Å metal structures," *Appl. Phys. Lett.* **29**, 596-598 (1 November 1976).

10. A. N. Broers and M. Pomerantz, "Rapid writing of fine lines in Langmuir-Blodgett films using electron beams," *Thin Solid Films*, **99**, 323-329 (1983); also, G. G. Roberts, "Langmuir-Blodgett films on semiconductors," pp. 56-67, Part II, Thin Insulating Films, in *Insulating Films on Semiconductors*, M. Schulz and G. Pensl, eds. (Springer-Verlag, Berlin 1981).

11. C. R. K. Marrian and R. J. Colton, "Low-voltage electron beam lithography with a scanning tunneling microscope," *Appl. Phys. Lett.* **56**, 755-757 (19 February 1990).

12. See, for example, J. D. Swalen, D. L. Allara, J. D. Andrade, E. A. Chandross, S. Garoff, J. Israelachvili, T. J. McCarthy, R. Murray, R. F. Pease, J. F. Rabolt, K. J. Wynne, and H. Yu, "Molecular monolayers and films," *Langmuir*, **3**, 932-950 (1987).

13. D. P. E. Smith, A. Bryant, C. F. Quate, J. P. Rabe, Ch. Gerber, and J. D. Swalen, "Images of a lipid bilayer at molecular resolution by scanning tunneling microscopy," *Proc. Natl. Acad. Sci. USA*, **84**, 969-972 (February 1987); also, C. A. Lang, J. K. H. Horber, T. W. Hansch, W. M. Heckl, and H. Mohwald, "Scanning tunneling microscopy of Langmuir-Blodgett films on graphite," *J. Vac. Sci. Technol. A* **6**, 368-370 (1988); also, H. G. Braun, H. Fuchs, and W. Schrepp, "Surface structure investigation of Langmuir-Blodgett films," *Thin Solid Films*, **159**, 301-314 (1988); also, W. Mizutani, M. Shigeno, K. Saito, K. Watanabe, M. Sugi, M. Ono, and K. Kajimura, "Observation of Langmuir-Blodgett films by scanning tunneling microscopy," *Jpn J. Appl. Phys.* **27**, 1803-1807 (1988).

14. H. Fuchs, S. Akari, and K. Dransfeld, "Molecular resolution of Langmuir-Blodgett monolayers on tungsten diselenide by scanning tunneling microscopy," *Z. Physik*, to be published.

15. R. Kuroda, E. Kishi, A. Yamano, K. Hatanaka, H. Matsuda, K. Eguchi, and T. Nakagiri, "Scanning tunneling microscope images of fatty acid LB bilayers," STM '90/NANO I, Baltimore, Md. July 23-27 1990 (to be published in *J. Vac. Sci. Technol. A*).

16. M.M. Dovek, T. R. Albrecht, S. W. J. Kuan, C. A. Lang, R. Emch, P. Grütter, C. W. Frank, R. F. W. Pease, and C. F. Quate, "Observation and manipulation of polymers by scanning tunnelling and atomic force microscopy," *J. Microsc.* **152**, 229-236 (October 1988).

17. H. Zhang, L. S. Hordon, S. W. J. Kuan, P. Maccagno, and R. F. W. Pease, "Exposure of ultrathin polymer resists with the scanning tunneling microscope," *J. Vac. Sci. Technol. B* **7**, 1717-1722 (Nov/Dec 1989).

18. T. R. Albrecht, M. M. Dovek, M. D. Kirk, C. A. Lang, C. F. Quate, and D. P. E. Smith, "Nanometer-scale hole formation on graphite using a scanning tunneling microscope," *Appl. Phys. Lett.* **55**, 1727-1729 (23 October 1989).

19. J. P. Rabe, S. Buchholz, and A. M. Ritcey, "Reactive graphite etch and the structure of an adsorbed organic monolayer - a scanning tunneling microscopy study," *J. Vac. Sci. Technol. A* **8**, 679-683 (Jan/Feb 1990).

20. J. S. Foster and J. E. Frommer, "Imaging of liquid crystals using a tunnelling microscope," *Nature*, **333**, 542-545 (9 June 1988); also, J. K. Spong, H. A. Mizes, L. J. La Comb, Jr., M. M. Dovek, J. E. Frommer, and J. S. Foster, "Contrast mechanism for resolving organic molecules with tunneling microscopy," *Nature*, **338**, 137-139 (9 March 1989).

21. W. Mizutani, M. Shigeno, M. Ono, and K. Kajimura, "Voltage-dependent scanning tunneling microscopy images of liquid crystals on graphite," *Appl. Phys. Lett.* **56**, 1974-1976 (14 May 1990).

22. D.P.E. Smith, H. Hörber, Ch. Gerber, and G. Binnig, "Smectic liquid crystal monolayers on graphite observed by scanning tunneling microscopy," *Science*, **245**, 43-45 (7 July 1989); also, D. P. E. Smith, J. K. H. Hörber, G. Binnig, and H. Nejoh, "Structure, registry and imaging mechanism of alkylcyanobiphenyl molecules by tunnelling microscopy," *Nature*, **344**, 641-644 (12 April 1990).

23. J. S. Foster, J. E. Frommer, and P. C. Arnett, "Molecular manipulation using a tunnelling microscope," *Nature*, **331**, 324-326 (28 January 1988).

24. R. H. Bernhardt, G. C. McGonigal, R. Schneider, and D. J. Thomson, "Mechanisms for the deposition of nanometer-sized structures from organic fluids using the scanning tunneling microscope," *J. Vac. Sci. Technol A* **8**, 667-671 (Jan/Feb 1990); also, G. C. McGonigal, R. H. Bernhardt, and D. J. Thomson, "Scanning tunnelling microscopy of ordered alkane layers adsorbed on graphite," *Appl. Phys. Lett.* **57**, 28-30 (1990).

25. R. Sonnenfeld and P. K. Hansma, "Atomic-resolution microscopy in water," *Science*, **232**, 211-213 (1986).

26. J. Schneir and P. K. Hansma, "Scanning tunneling microscopy and lithography of solid surfaces covered with nonpolar liquids," *Langmuir*, **3**, 1025-1027 (1987)

27. R. Sonnenfeld and B. C. Schardt, "Tunneling microscopy in an electrochemical cell: images of Ag plating," *Appl. Phys. Lett.* **49**, 1172-1174 (3 November 1986).

28. C. W. Lin, F-R. F. Fan, and A. J. Bard, "High resolution photoelectrochemical etching of n-GaAs with the scanning electrochemical and tunneling microscope," *J. Electrochem. Soc.* **134**, 1038-1039 (April 1987).

29. P. A. Kohl, C. Wolowodiuk, and F. W. Ostermayer, Jr., "The photoelectrochemical oxidation of (100), (111), and ($\bar{1}\bar{1}\bar{1}$) n-InP and n-GaAs," *J. Electrochem. Soc: Solid-State Sci. Technol.* **130**, 2288-2293 (November 1983).

30. F. W. Ostermayer, Jr. and P. A. Kohl, "Photoelectrochemical etching of *p*-GaAs," *Appl. Phys. Lett.* **39**, 76-78 (1 July 1981).

31. R. M. Lum, A. M. Glass, F. W. Ostermayer, Jr., P. A. Kohl, A. A. Ballman, and R. A. Logan, "Holographic photoelectrochemical etching of diffraction gratings in *n*-InP and *n*-GaInAsP for distributed feedback lasers," *J. Appl. Phys.* **57**, 39-44 (1 January 1985).

32. J. J. Ritsko, "Laser etching," Chap 6, 363-383, in *Laser Microfabrication*, D. J. Ehrlich and J. Y. Tsao, eds. (Academic Press, Inc. New York 1989).

33. L. A. Nagahara, T. Thundat, and S. M. Lindsay, "Nanolithography on semiconductor surfaces under solution using scanning tunneling microscopy," STM '90/NANO I, Baltimore, Md. July 23-27 1990 (to be published in *J. Vac. Sci. Technol. A*).

34. L. A. Nagahara, T. Thundat, and S. M. Lindsay, "Preparation and characterization of STM tips for electrochemical studies," *Rev. Sci. Instrum.* **60**, 3128-3130 (October 1989).

35. L. A. Nagahara, T. Thundat and S. M. Lindsay, "Nanolithography on semiconductor surfaces under an etching solution," *Appl. Phys. Lett.* **57**, 270-272 (16 July 1990).

36. E. J. van Loenen, D. Dijkkamp, A. J. Hoeven, J. M. Lenssinck, and J. Dieleman, "Direct writing in Si with a scanning tunneling microscope," *Appl. Phys. Lett.* **55**, 1312-1314 (25 September 1989).

37. M. Iwatsuki, private communication; also, M. Iwatsuki, S. Kitamura, and A. Mogami, "Development of the UHV-STM," in *Proceedings XIIth Intl. Congress for Elec. Microscopy*, pp. 322-323 (San Francisco Press, Inc, San Francisco, 1990).

38. F. Besenbacher and K. Mortensen, to be published.

39. Ph. Avouris, private communication.

40. R. E. Kirby and D. Lichtman, "Electron beam induced effects on gas absorption utilizing auger electron spectroscopy: CO and O_2 on Si," *Surf. Sci.* **41**, 447-466 (1974); also, J. P. Coad, H. E. Bishop, and J. C. Riviere, "Electron-beam assisted adsorption on the Si(111) surface," *Surf. Sci.* **21**, 253-264 (1970).

41. J. A. Dagata, J. Schneir, H. H. Harary, C. J. Evans, M. T. Postek, and J. Bennett, "Modification of hydrogen-passivated silicon by a scanning tunneling microscope operating in air," *Appl. Phys. Lett.* **56**, 2001-2003 (14 May 1990); also, J. A. Dagata, J. Schneir, H. H. Harary, J. Bennett, and W. Tseng, "Pattern generation on semiconductor surfaces by a scanning tunneling microscope operating in air," STM '90/NANO I, Baltimore, Md. July 23-27 1990 (to be published in *J. Vac. Sci. Technol. A*).

42. F. J. Grunthaner and P. J. Grunthaner, "Chemical and electronic structure of the SiO_2/Si interface," *Matl. Sci. Rep.* **1**, 65-160 (1986).

43. D. B. Fenner, D. K. Biegelsen, and R. D. Bringans, "Silicon surface passivation by hydrogen termination: a comparative study of preparation methods," *J. Appl. Phys.* **66**, 419-424 (1989).

44. W. J. Kaiser, L. D. Bell, M. H. Hecht, and F. J. Grunthaner, "Scanning tunneling microscopy characterization of the geometric and electronic structure of hydrogen-terminated surfaces," *J. Vac. Sci. Technol. A* **6**, 519-523 (1988).

45. U. Staufer, R. Wiesendanger, L. Eng, L. Rosenthaler, H. R. Hidber, H. -J. Güntherodt, and N. Garcia, "Nanometer scale structure fabrication with the scanning tunneling microscope," *Appl. Phys. Lett.* **51**, 244-246 (1987); also, U. Staufer, R. Wiesendanger, L. Eng, L. Rosenthaler, H. R. Hidber, H. -J. Güntherodt, and N. Garcia, "Surface modification in the nanometer range by the scanning tunneling microscope," *J. Vac. Sci. Technol. A* **6**, 537-539 (Mar/Apr 1988); also, U. Staufer, L. Scandella, and R. Wiesendanger, "Direct writing of nanometer scale structures on glassy metals by the scanning tunneling microscope," *Z. Physik B - Condensed Matter*, **77**, 281-286 (1989).

46. P. Chaudhari, J. J. Cuomo, and R. J. Gambino, "Amorphous metallic films for magneto-optic applications," *Appl. Phys. Lett.* **22**, 337-339 (1 April 1973); also,

J. C. Suits, D. Rugar, and C. J. Lin, "Thermomagnetic writing in Tb-Fe: modeling and comparison with experiment," *J. Appl. Phys.* **64**, 252-261 (1 July 1988).

47. J. Jahanmir, P. E. West, S. Hsieh, and T. N. Rhodin, "Surface modification of *a*-Si:H with a scanning tunneling microscope operated in air," *J. Appl. Phys.* **65**, 2064-2068 (1 March 1989).

48. R. Wiesendanger, L. Rosenthaler, H. R. Hidber, H. -J. Güntherodt, A. W. McKinnon, and W. E. Spear, "Hydrogenated amorphous silicon studied by scanning tunneling microscope," *J. Appl. Phys.* **63**, 4515-4517 (1 May 1988).

49. E. Hartmann and F. Koch, private communication.

50. J. S. Foster, K. A. Rubin, and D. Rugar, "Data storage method using state transformable materials," US Patent No. 4,916,688 (April 10, 1990).

51. J. Moreland and P. Rice, "High-resolution, tunneling-stabilized magnetic imaging and recording," *Appl. Phys. Lett.* **57**, 310-312 (16 July 1990).

52. S. Iwamura, Y. Nishida, and K. Hashimoto, "Rotating MNOS Disk Memory Device," *IEEE Trans. Electron Devices*, **ED-28**, 854-860 (July 1981).

53. J. J. Chang, "Nonvolatile semiconductor memory devices," *Proc. IEEE*, **64**, 1039-1059 (July 1976).

54. M. M. E. Beguwala, and T. L. Gunckel, II, "An improved model for the charging characteristics of a dual-dielectric (MNOS) nonvolatile memory device," *IEEE Trans. Electron Devices*, **ED-25**, 1023-1030 (August 1978).

55. J. E. Brewer, "MNOS density parameters," *IEEE Trans. Electron Devices*, **ED-24**, 618-625 (May 1977).

56. R. S. Withers, R. W. Ralston, and E. Stern, "Nonvolatile analog memory in MNOS capacitors," *IEEE Electron Dev. Lett.* **EDL-1**, 42-45 (March 1980).

57. Work relating to this project has been reported by J. E. Stern, B. D. Terris, H. J. Mamin, and D. Rugar, "Deposition and imaging of localized charge on

insulator surfaces using a force microscope," *Appl. Phys. Lett.* **53**, 2717-2719 (26 December 1988).

58. D. J. Ehrlich, R. M. Osgood, Jr., and T. F. Deutsch, "Photodeposition of metal films with ultraviolet laser light," *J. Vac. Sci. Technol.* **21**, 23-32 (May/June 1982); also, D. V. Podlesnik, H. H. Gilgen, and R. M. Osgood, Jr., "Waveguiding effects in laser-induced aqueous etching of semiconductors," *Appl. Phys. Lett.* **48**, 496-498 (17 February 1986); also, H. S. Cole, Y. S. Liu, J. W. Rose, and R. Guida, "Laser-induced selective copper deposition on polyimide," *Appl. Phys. Lett.* **53**, 2111-2113 (21 November 1988); also, R. J. von Gutfeld, "Laser-enhanced patterning using photothermal effects: maskless plating and etching," *J. Opt. Soc. Am. B* **4**, 272-279 (February 1987).

59. S. Matsui and K. Mori, "New selective deposition technology by electron beam induced surface reaction," *J. Vac. Sci. Technol. B* **4**, 299-304 (Jan/Feb 1986).

60. S. Matsui and T. Ichihashi, "*In situ* observation on electron-beam-induced chemical vapor deposition by transmission electron microscopy," *Appl. Phys. Lett.* **53**, 842-844 (5 September 1988).

61. S. Matsui, "Electron beam lithography using surface reactions with ClF_3," *Appl. Phys. Lett.* **55**, 134-136 (10 July 1989).

62. R. M. Silver, E. E. Ehrichs, and A. L. de Lozanne, "Direct writing of submicron metallic features with a scanning tunneling microscope," *Appl. Phys. Lett.* **51**, 247-249 (27 July 1987), also, E. E. Ehrichs, R. M. Silver, and A. L. de Lozanne, "Direct writing with the scanning tunneling microscope," *J. Vac. Sci. Technol. A* **6**, 540-543 (Mar/Apr 1988).

63. M. A. McCord, D. P. Kern, and T. H. P. Chang, "Direct deposition of 10-nm metallic features with the scanning tunneling microscope," *J. Vac. Sci. Technol. B* **6**, 1877-1880 (Nov/Dec 1988).

64. D. D. Awschalom, M. A. McCord, and G. Grinstein, "Observation of macroscopic spin phenomena in nanometer-scale magnets," *Phys. Rev. Lett.* **65**, 783-786 (6 August 1990).

65. D. D. Awschalom, J. R. Rozen, M. B. Ketchen, W. J. Gallagher, A. W. Kleinsasser, R. L. Sandstrom, and B. Bumble, "Low-noise modular microsusceptometer using nearly quantum limited dc SQUIDs," *Appl. Phys. Lett.* **53**, 2108-2110 (21 November 1988).

66. D. M. Eigler and E. K. Schweizer, "Positioning single atoms with a scanning tunneling microscope," *Nature*, **344**, 524-526 (5 April 1990).

67. G. R. Hennig, "Electron microscopy of reactivity changes near lattice defects in graphite," in *Chemistry and Physics of Carbon*, vol. 2, P. L. Walker, Jr., ed. pp. 1-49, Marcel Dekker, Inc., New York (1966); also, R. T. Yang, "Etch-decoration electron microscopy studies of the gas-carbon reactions," in *Chemistry and Physics of Carbon*, vol. 19, P. A. Thrower, ed. pp. 163-210, Marcel Dekker, Inc., New York (1984).

68. R. T. Yang, *loc. cit.*

69. H. Chang and A. J. Bard, "Formation of monolayer pits of controlled nanometer size on highly oriented pyrolytic graphite by gasification reactions as studied by scanning tunneling microscopy," *J. Am. Chem. Soc.* **112**, 4598-4599 (1990).

70. C. I. H. Ashby and R. R. Rye, "Electron enhanced hydrogen attack on first wall materials," *J. Nucl. Matl.* **103 & 104**, 489-492 (1981).

71. A. A. Haasz, P. C. Stangeby, and O. Auciello, "Methane production from graphite and TiC under electron and atomic hydrogen impact," *J. Nucl. Matl.* **111 & 112**, 757-762 (1982).

72. G. R. Hennig, *loc. cit.*

73. J. J. Hren, "Barriers to AEM: contamination and etching," in *Analytical Electron Microscopy*, J. J. Hren, D. Joy, and J. I. Goldstein, eds. Chap. 18, pp. 481-505, Plenum Press, New York (1985).

74. R. F. Egerton and C. J. Rossouw, "Direct measurement of contamination and etching rates in an electron beam," *J. Phys. D: Appl. Phys.* **9**, 659-663 (1976).

75. K. Terashima, M. Kondoh, and T. Yoshida, "Fabrication of nucleation sites for nanometer size selective deposition by scanning tunneling microscope," *J. Vac. Sci. Technol. A* **8**, 581-584 (Jan/Feb 1990).

76. W. Mizutani, J. Inukai, and M. Ono, "Making a monolayer hole in a graphite surface by means of a scanning tunneling microscope," *Japn J. Appl. Phys.* **29**, L815-L817 (May 1990).

77. T. C. Shen, R. T. Brockenbrough, J. S. Hubacek, J. R. Tucker, and J. W. Lyding, "Ion irradiation effects on graphite with the scanning tunneling microscope," STM '90/NANO I, Baltimore, Md. July 23-27 1990 (to be published in *J. Vac. Sci. Technol. A*).

78. Bernhardt, *loc. cit.*

79. Rabe, *loc. cit.*

80. R. M. Penner, M. J. Heben, N. S. Lewis, and C. F. Quate, "Mechanistic investigations of STM lithography at liquid-covered graphite surfaces," to be published.

81. H. J. Mamin, P. H. Guethner, and D. Rugar, "Atomic emission from a gold scanning tunneling microscope tip," to be published.

82. E. W. Müller and T. T. Tsong, in *"Field Ion Microscopy, Principles and Applications,"* Elsevier, New York (1969).

83. J. K. Gimzewski and R. Möller, "Transition from the tunneling regime to point contact studied using scanning tunneling microscopy," *Phys. Rev B* **36**, 1284-1287 (15 July 1987).

84. J. P. Rabe and S. Buchholz, "Fast nanoscale modification of Ag(111) by STM," to be published.

85. S. Buchholz, H. Fuchs, and J. P. Rabe, "Characterization of thin evaporated metallic films by STM, SEM and LEED," STM '90/NANO I, Baltimore, Md. July 23-27 1990 (to be published in *J. Vac. Sci. Technol A*).

86. R. C. Jaklevic and L. Elie, "Scanning-tunneling-microscope observation of surface diffusion on an atomic scale: Au on Au(111)," *Phys. Rev. Lett.* **60**, 120-123 (11 January 1988).

87. R. C. Jaklevic, private communication.

88. J. Schneir, R. Sonnenfeld, O. Marti, P. K. Hansma, J. E. Demuth, and R. J. Hamers, "Tunneling microscopy, lithography, and surface diffusion on an easily prepared, atomically flat gold surface," *J. Appl. Phys.* **63**, 717-721 (1988); also J. Schneir and P. K. Hansma, "Scanning tunneling microscopy and lithography of solid surfaces covered with nonpolar liquids," *Langmuir*, **3**, 1025-1027 (1987).

89. T. Hsu and J. M. Cowley, "Reflection electron microscopy (REM) of fcc metals," *Ultramicroscopy*, **11**, 239-250 (1983).

90. Y. Z. Li, L. Vazquez, R. Piner, R. P. Andres, and R. Reifenberger, "Writing nanometer-scale symbols in gold using the scanning tunneling microscope," *Appl. Phys. Lett.* **54**, 1424-1426 (10 April 1989); also, US Patent No. 4,896,044 (January 23, 1990).

91. T. Hsu and J. M. Cowley, *loc. cit.*

92. R. Emch, J. Nogami, M. M. Dovek, C. A. Lang, and C. F. Quate, "Characterization of gold surfaces for use as substrates in scanning tunneling microscopy studies," *J. Appl. Phys.* **65**, 79-84 (1 January 1989).

93. K. Reichelt and H. O. Lutz, "Hetero-epitaxial growth of vacuum evaporated silver and gold," *J. Crystal Growth*, **10**, 103-107 (1971); also, V. M. Hallmark, S. Chiang, J. F. Rabolt, J. D. Swalen, and R. J. Wilson, "Observation of atomic corrugation on Au(111) by scanning tunneling microscopy," *Phys. Rev. Lett.* **59**, 2879-2882 (21 December 1987); also, E. Holland-Moritz, J. Gordon II, G. Borges, and R. Sonnenfeld, "Motion of atomic steps of Au(111) films on mica," to be published.

94. R. C. Jaklevic, private communication.

95. M. Francois, K. Pourrezaei, A. Bahasadri, and D. Nayak, "Investigation of the liquid metal ion source cluster beam constituents and their role in the properties of the deposited film," *J. Vac. Sci. Technol. B* **5**, 178-183 (Jan/Feb 1987).

96. R. L. Seliger, J. W. Ward, V. Wang, and R. L. Kubena, "A high-intensity scanning ion probe with submicrometer spot size," *Appl. Phys. Lett.* **34**, 310-312 (1 March 1979).

97. J. Puretz, R. K. DeFreez, R. A. Elliott, and J. Orloff, "Focused-ion-beam micromachined AlGaAs semiconductor laser mirrors," *Electron. Lett.* **22**, 700-702 (19 June 1986).

98. R. Gomer, "On the mechanism of liquid metal electron and ion sources," *Appl. Phys.* **19**, 365-375 (1979).

99. G. I. Taylor, "Disintegration of water drops in an electric field," *Proc. Roy. Soc. London*, Ser. A, **280**, 383-397 (1964).

100. A. E. Bell, private communication.

101. G. Ben Assayag and P. Sudraud, "LMIS energy broadening interpretation supported by HV-TEM observations," *J. de Phys.* Colloque C9, Tome 45, C9-223-226 (December 1984).

102. L. W. Swanson, G. A. Schwind, A. E. Bell, and J. E. Brady, "Emission characteristics of gallium and bismuth liquid metal field ion sources," *J. Vac. Sci. Technol.* **16**, 1864-1867 (Nov/Dec 1979).

103. A. Wagner and T. M. Hall, "Liquid gold ion source," *J. Vac. Sci. Technol.* **16**, 1871-1874 (Nov/Dec 1979); also, A. Wagner, "The hydrodynamics of liquid metal ion sources," *Appl. Phys. Lett.* **40**, 440-442 (1 March 1982).

104. A. E. Bell, K. Rao, and L. W. Swanson, "Scanning tunneling microscope liquid-metal ion source for microfabrication," *J. Vac. Sci. Technol. B* **6**, 306-310 (Jan/Feb 1988); also, G. Ben Assayag, P. Sudraud, and L. W. Swanson, "Close-spaced ion emission from gold and gallium liquid metal ion source," *Surf. Sci.* **181**, 362-369 (1987).

105. T. T. Tsong, in *Atom-probe field ion microscopy*, Cambridge Univ. Press, Cambridge (1990).

106. E. W. Müller, J. A. Panitz, and S. B. McLane, "The atom-probe field ion microscope," *Rev. Sci. Instrum.* **39**, 83-86 (January 1968).

107. J. A. Panitz, "The 10 cm atom probe," *Rev. Sci. Instrum.* **44**, 1034-1038 (August 1973).

108. E. W. Müller, "Field ionization and field ion microscopy," in *Advances in Electronics and Electron Physics*, vol. XIII, pp. 83-179 (Academic Press Inc. New York, 1960).

109. E. W. Müller, "Field desorption," *Phys. Rev.* **102**, 618-624 (May 1 1956).

110. R. Gomer and L. W. Swanson, "Theory of field desorption," *J. Chem. Phys.* **38**, 1613-1629 (1 April 1963).

111. T. T. Tsong, "Studies of solid surfaces at atomic resolution-atom-probe and field ion microscopy," *Surf. Sci. Rep.* **8**, 127-209 (North-Holland, Amsterdam, 1988).

112. "One meter of atoms per second" is the rate of removal of atoms from a surface in the Atom Probe, so it is not surprising to observe atomic layers removed in nanoseconds; J. Panitz, private communication.

113. H. J. Mamin, S. Chiang, H. Birk, P. H. Guethner, and D. Rugar, "Gold deposition from a scanning tunneling microscope tip," STM '90/NANO I, Baltimore, Md. July 23-27 1990 (to be published in *J. Vac. Sci. Technol. A*); also, H. J. Mamin, P. H. Guethner, and D. Rugar, "Atomic emission from a gold scanning-tunneling-microscope tip," *Phys. Rev. Lett.* **65**, 2418-2421 (5 November 1990).